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CONTRACT REPORT

FINAL REPORT P-3543/G-7

Investigation of the Application of Wet Oxidation Technology to the Dewatering and Combustion of Peat

Contract: DSS 18SQ.23440-0-9081

ONTARIO RESEARCH FOUNDATION

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Investigation of the Application of Wet Oxidation Technology to the Dewatering and Combustion of Peat

Contract: DSS 18SQ.23440-0-9081

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Peat bogs may cover a large portion of Canada's surface, but obtaining a few tons of wet peat of specified quality can be surprisingly difficult. We are grateful to Messrs. R. Fleming of Fisons-Western Peat Ltd., R. Kristjansson of the Ontario Ministry of Natural Resources, and D. Rees of Noval Technologies Ltd. who helped us obtain large samples of raw peat.

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Investigation of the Application of
Wet Oxidation Technology to the
Dewatering and Combustion of Peat

(Proposal P-3543/G)

Contract: DSS 18SQ.23440-0-9081

SUMMARY

In the course of batch autoclave and continuous flow pilot plant experiments, a two-stage, consecutive first order reaction model was assumed and tested for the wet combustion of medium to highly humified peat.

Batch autoclave and continuous flow pilot plant experiments identified the autothermal partial oxidation reactor conditions which result in a mechanically dewaterable (up to 50% moisture) peat solid mass.

The solubilized peat mass present in the wastewaters of the above reactions is easily treatable in an anaerobic filter type reactor, resulting in further energy recovery in the form of digester gas containing up to 75% methane.

Final treatment of the digester effluents was found to be practicable in an extended aeration type of activated sludge system. Full nitrification and BOD_5 removal to < 50 mg/L effluent concentration was found to be achievable.

The above unit processes were integrated into three systems and evaluated as case studies for mass, energy and economic balance on the scale of 50 tonnes wet peat feed per hour. The case studies optimized reactor conditions for feed concentrations ranging from 3.7 to 11% solids and evaluated capital and product costs for a range of feed costs from $0.40 to $4.80 per wet tonne of wet-mined peat. Financing conditions assumed 20 years of plant life, zero salvage value and 18% interest on capital. The case studies established that:

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1. Thermal energy generation through a combination of wet oxidation and anaerobic digestion of 150 g COD/litre (∿ 11% solids) feed will yield 27.7 MW energy at the cost of $6.04 and $8.50/GJ for the extremes of feedstock cost. Capital investment is estimated to be $404 per kW output capacity. Thermal efficiency was 55.4%.

2. Electric energy generation through a combination of wet oxidation, anaerobic digestion and a turbine-generator will yield 1.9 MWe from 50 g COD/L (∿ 3.6% solids) feed. The cost of electricity is $0.140 and $0.258 for $0.40 and $4.80 per tonne feedstock, respectively. Thermal efficiency of conversion is 18.6%. Capital investment is $3,842 per kWe output capacity.

3. Solid peat fuel could be produced through the autothermal partial wet oxidation of peat. The methane produced through anaerobic digestion of the effluents will dry the product to a final moisture content of 33% without the need for additional fuel. From 50 wet tonnes/hour feed at 150 g COD/L (∿ 11% solids) concentration, the process will yield 3.3 dry tonnes/hour product at the cost of $3.92 or $7.31/GJ for the low and high extremes of feed peat cost. These values were calculated for a dry product heating value of 21.8 GJ/kg. Capital expenditures for this scale of operation and feed concentration would be $8.65 x 10^6.

It is recommended that Cases 2 and 3 and an additional one optimized for methane generation be considered for further development.

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1. INTRODUCTION

Peat bogs cover 12 percent of Canada and may have an energy content greater than all of our known fossil fuel reserves, excluding the tar sands. However, on account of competition from more easily available fuels and certain technical problems regarding the exploitation of peat, none of this immense energy potential is presently contributing to the country's energy economy.

The most difficult technical obstacle to utilizing peat as a raw material or fuel is the reduction of its high associated water content. Peat, as found in nature, may contain over 90% water. This moisture content must be reduced to below 50% before peat can be burned in conventional combustion equipment.

The methods generally utilized to this end at present make use of solar energy at the time of mining to reduce the water content to 30-50%. These are the well-known milled peat and sod peat mining techniques, which allow the mined peat to dry on the surface of the bog before being collected and used.

In many situations, this may be adequate. There are others where the potential drawbacks force a look for alternative ways of mining and processing:

- The climate and weather at the peat mine do not allow an economical production season.
- The scale of the proposed operation would necessitate an inordinately large area to be worked, since only a thin layer of the bog surface can be mined each season (e.g. $\sim$ 20 cm/yr for milled peat in many parts of Ontario).
- There are environmental problems associated with these mining methods: wind-borne dust, interruption of natural environments for 20 years or more, possibility of bog fires.

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To get around the dependence on solar power for drying the peat, wet mining has been proposed. Peat would be extracted with its associated moisture content and transported via pipeline or conveyor belt to the processing plant nearby.

The technologies for processing wet-mined peat are distinct from those utilizing solar dried material. Several of these are in laboratory scale development, and one process (wet carbonization) is in the early stages of commercialization.

The process investigated in this project consists of combusting fuel peat, in the presence of the associated bog-water by the Wetox(R) process. If total combustion is aimed at, energy may be recovered in the form of steam and hot water or electricity. It is also possible to oxidize only a part of the peat feedstock, generate sufficient energy to carry out the wet carbonization reaction on the balance of the feed and recover a combustible solid fuel which may be mechanically dewatered to less than 50% moisture content. Residual dissolved or dispersed organic material is further processed by anaerobic digestion to yield energy in the form of combustible biogas (methane and carbon dioxide).

The overall objective of this program was to determine the technical and economic feasibility of two routes applied to the processing of wet-mined peat. These two processing routes consisted of:

(a) the complete oxidation of wet peat for energy recovery.

(b) the partial, autothermal oxidation of the feed peat to achieve the breakdown of its water-retaining properties, thus enabling the production of solid fuel by mechanical dewatering.

Since an appreciable amount of the peat is solubilized both in the total and partial oxidation processes, the resulting wastewater must be treated before discharge into the environment. Anaerobic digestion allows the possibility of recovering biogas from the wastewater. The biogas can improve the overall energy balance of both process alternatives. Therefore, the wastewater treatment aspects were integrated into the experimental program and the economc evaluation.

The stages of experimental and design work are listed in Table 1.1. The total oxidation experiments were carried out on three different peat samples. Partial oxidation and dewatering was investigated using one peat sample.

TABLE 1.1 - Project Outline

Task 1 Peat Wet Mining Costs

- Survey of wet mining methods
- Summary of published costs for wet-mined peat

Task 2 Total Oxidation

- Examination of wet combustion kinetics in batch autoclave experiments
- Assumption of a kinetic model of peat wet combustion
- Scale-up of batch tests to continuous flow, pilot scale processing

Task 3 Partial Oxidation

- Experimental verification of the concept of wet carbonization combined with partial oxidation in a batch autoclave
- Derivation of experimental parameters for continuous processing on the pilot plant scale
- Continuous flow partial oxidation pilot plant experiments

Task 4 Wastewater Treatment

- Determination of the anaerobic digestibility of the wastewaters of total oxidation
- Determination of energy recovery in the form of biogas
- Aerobic treatability study of the effluent from anaerobic digestion

Task 5 Process Simulation

- Computer simulation of the mass and energy balance of three process configurations:

  Case 1: Total wet oxidation of peat, producing thermal energy

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Case 2: Total wet oxidation of peat, generating electrical energy

Case 3: Partial wet oxidation, wet carbonization and dewatering of peat to produce a solid fuel.

Task 6 Economic Evaluation

- Evaluation of product costs for a range of process and economic conditions, for all three cases.

2. LITERATURE REVIEW

2.1 A Brief Description of Wet Oxidation

2.1.1 History of Wet Air Oxidation

Wet air oxidation is not a new process - patents in the fields of extractive metallurgy and waste treatment were granted at the turn of the century. The extractive metallurgical applications originated from the Bayer Process which was patented in 1888. The application of wet air oxidation to waste treatment proceeded from R. W. Strehlenert who, in 1915, patented a process for the treatment of spent pulping liquors with oxygen at elevated temperatures and pressures. Development of the process proceeded simultaneously in several fields and in many countries, including Sweden, Germany and U.S.A.

Cederquist, using a horizontal, agitated autoclave, investigated the use of wet oxidation for energy production from peat, wood, spent pulping liquor, etc. He published his findings in 1953, and 1955. It was at this time that W. K. Porteus was applying for patents concerning various applications of the Porteus Process or "heat treatment". In 1954, F. J. Zimmerman was granted a patent for the destructive oxidation of organic material in liquid waste effluents. Soon after, the Sterling Drug Company founded the Zimpro Division of that corporation to market the Zimmerman Process. In this process, the reaction is carried out in a vertical tower reactor.

In 1952, plans were announced by the Chemical Construction Company, then a subsidiary of American Cyanamid Company, for the exploitation of a new process for the pressure leaching of metallurgical materials. Plants were under construction, at that time, for three firms: Sherritt Gordon Mines Ltd., National Lead Company and the Calera Mining Company. The Wetox(R) Process originated from the Calera Mining Company wet oxidation process constructed in 1954. The Calera process used a horizontal, multi-compartmented autoclave to react cobalt ore and oxygen at 204°C. The Calera autoclave routinely treated a slurry with a COD equivalent of greater than 30%.

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2.1.2 Fundamentals of Wet Air Oxidation

Wet air oxidation is a process in which combustible material is oxidized by air or oxygen in the presence of liquid water. Elevated temperatures are required to achieve a useful reaction rate and, therefore, to maintain a liquid phase, elevated pressures are required. The process is operated continuously with liquid and gas streams being introduced to the reactor simultaneously.

A basic flowsheet for the process is presented in Figure 2.1. The waste is pumped via a high pressure pump through a heat exchanger and then into a reactor where it is mixed with compressed air. The oxygen in the air reacts with the organic matter in the slurry to produce mainly carbon dioxide and water. Due to the exothermic nature of the reaction, heat is produced which raises the temperature of the reactor contents. The effluent from the wet oxidation reactor is heat exchanged with the incoming waste.

Almost any combustible material which remains in the liquid phase can be oxidized in the process. The destruction of the organic contaminants is achieved as well in water at elevated temperature and pressure as by concentrating the material and incinerating the dry residue. In either case the products are the same: carbon dioxide, water and ash. Since the products from wet air oxidation are automatically and thoroughly scrubbed, air and odour pollution are minimized.

The wet air oxidation process provides an efficient means for the recovery of the energy from relatively dilute waste streams. The reaction occurs and the energy is liberated in the liquid phase, with no barrier to the transfer. The energy can, therefore, be recovered with the highest degree of efficiency.

2.1.3 Physical Parameters Governing Wet Oxidation

The maximum extent of the oxidation is primarily a function of the maximum operating temperature within the reactor. A typical combustion curve is presented in Figure 2.2. The operating

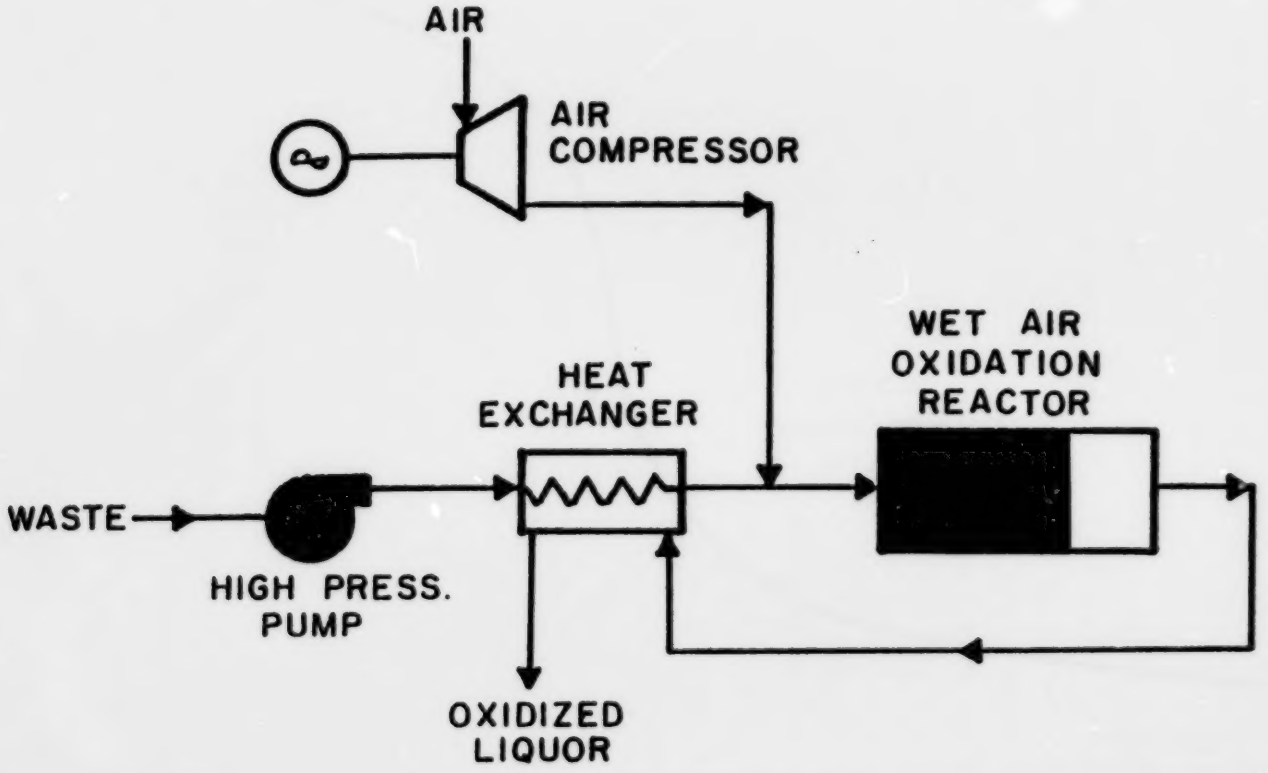

FIGURE 2.1 - General Wet Combustion Schematic

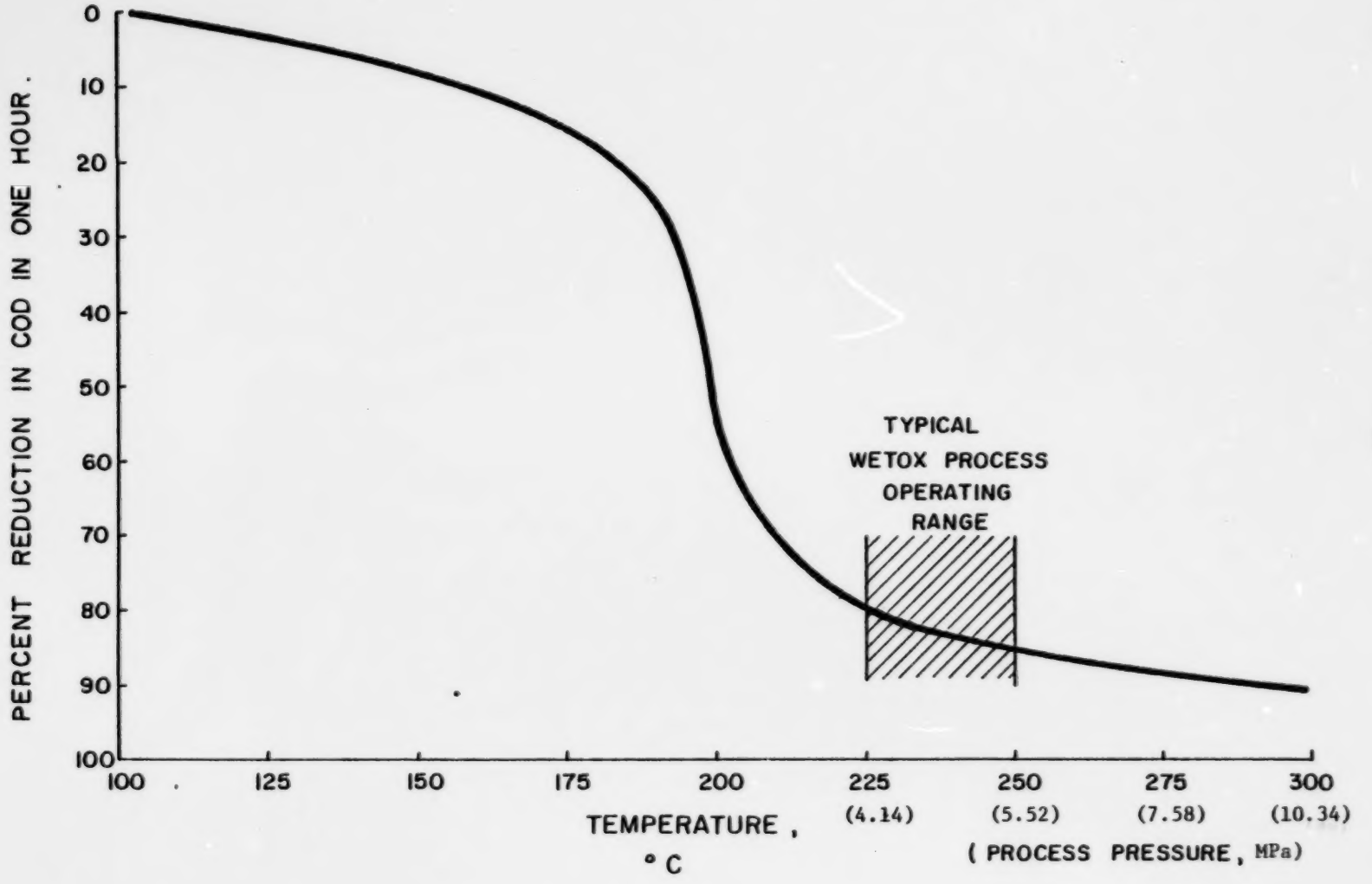

FIGURE 2.2 - Effect of Temperature

temperature effectively dictates the minimum operating pressure since confinement of the resulting steam and adequate oxygen partial pressure is required.

In wet air oxidation, oxidation and hydrolysis reactions proceed simultaneously depending on the availability of oxygen. Thus, with inadequate transfer of oxygen, hydrolysis reactions become significant and often generate products which are refractory to further oxidation in this process. Examples of these products are low molecular weight carboxylic acids; acetic, propionic, etc. The mass transfer requirements must, therefore, be satisfied to achieve maximum conversions to carbon dioxide and water. The rate of transfer of oxygen into the solution at a given operating temperature is controlled by:

- The solubility of oxygen in the waste which is a function of the oxygen partial pressure or over-pressure. Increased process pressures will, therefore, result in increased rates of mass transfer.
- The degree of mixing of the oxygen and the waste.

Increased process pressures result in increased capital costs for the reactor vessel, heat exchanger, compressor, etc., as well as increased operating costs, largely attributable to electrical power consumption. Effective mixing is, therefore, a most important parameter in economically optimizing the system, as shown in Figure 2.3.

2.1.4 Applications of Wet Air Oxidation

The process is uniquely suited to the oxidation of waste liquors, slurries and sludges where the organic matter is but a few percent of the predominantly water stream. The relative position of wet air oxidation in relation to conventional wastewater treatment techniques is shown in Figure 2.4. It is the most economical process for wastes which have a concentration of oxidizable material between 2 and 20% by weight with water.

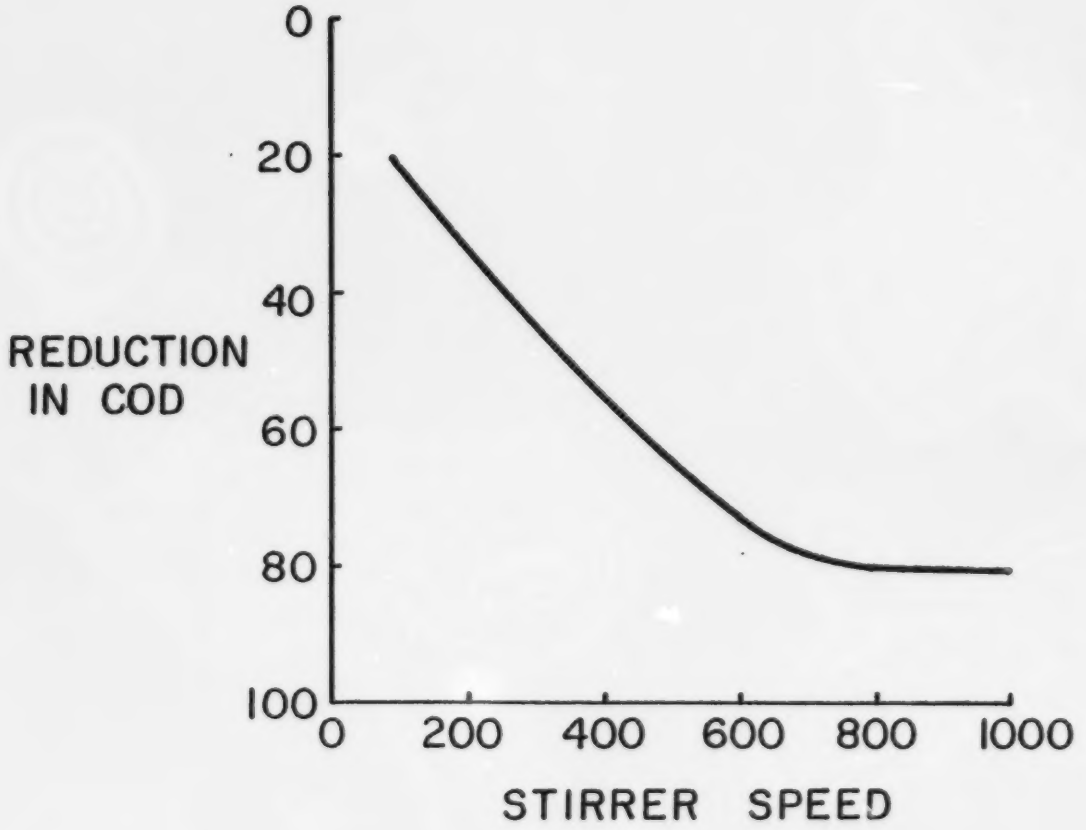

FIGURE 2.3 - Effect of Stirring

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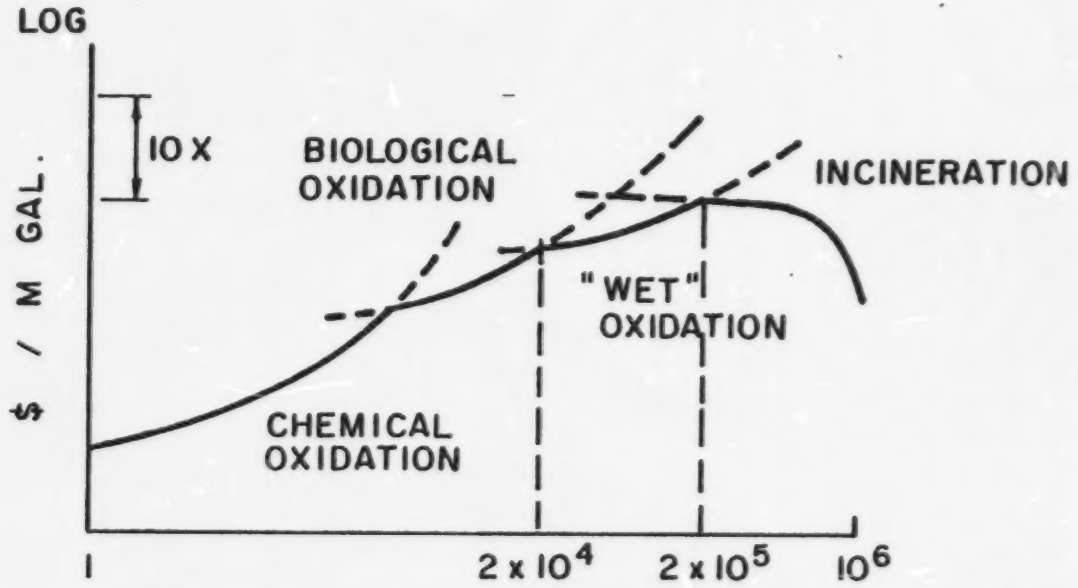

FIGURE 2.4 - Comparison of Total Waste Disposal Costs

In this range, sufficient material is available to react with the oxygen to generate enough heat to maintain the desired temperature and pressure in the reactor without external energy being supplied. Above about 1.5% concentration, excess heat is generally produced which can be efficiently and economically recovered. Above 20% concentration, incineration would generally be the most efficient method of disposal. Wet air oxidation is, therefore, most effective on wastes too concentrated for biological or chemical oxidation and too dilute for incineration.

Wet air oxidation can be applied to non-biodegradable materials as well as dangerous, toxic or noxious wastes. Valuable inorganic materials can be efficiently recovered from the liquid phase effluent. This is especially important for materials which after incineration would not be in a recoverable or reusable form. Because the oxidation takes place under water, the production of air and odour pollution is minimized. Potentially noxious materials remain in solution and exit the reactor in the liquid phase as salts or acids such as sulfates, chlorides, etc.

Other Process applications include:

- Conversion of agricultural residues to single cell protein and/or methane via wet oxidation and biological treatment.
- Desulfurization of high sulfur fuels such as lignite, coal, coke, etc.
- Combustion of low-grade fuels such as peat, low-grade coal, waste paper, etc.
- Regeneration of activated carbon.

2.1.5 The Wetox Process

The heart of the Wetox Process (see Figure 2.5) is the reactor: a multi-compartmented horizontal unit with agitation and oxygen addition in each compartment. This design results in substantially increased reaction rates and makes possible efficient operation at relatively modest temperatures and pressures ($\sim$ 230°C and $\sim$ 4.14 MPa).

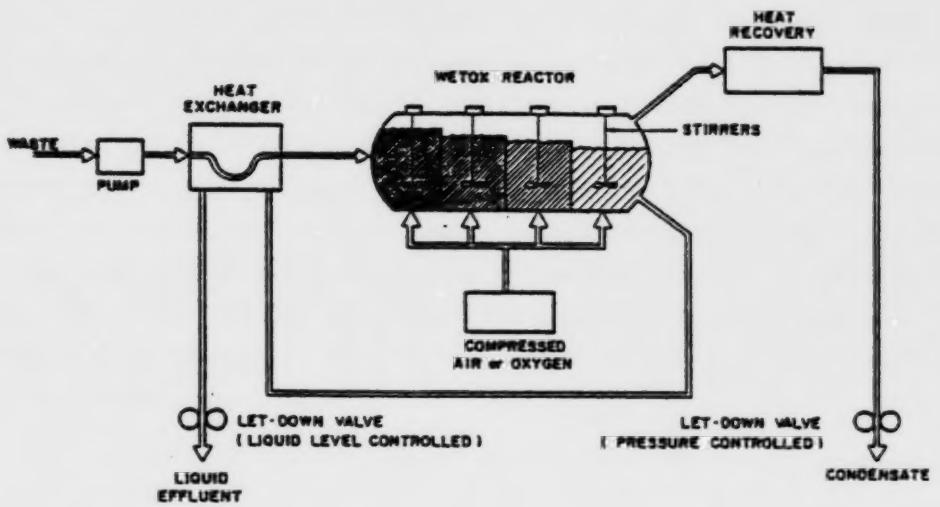

FIGURE 2.5 - Wetox(R) Process Schematic

The liquid and steam phases are withdrawn separately from the reactor. This feature improves the heat exchanger efficiency, increases the effective retention time of the liquid, and reduces the volume of liquid effluent for chemical recovery or treatment.

2.2 Wet Oxidation of Peat

Subjecting aqueous peat slurries to oxidation, either partial or complete, has not been extensively researched.

The only experimental data on the subject were published by Cederquist. He originally proposed the concept of partially oxidizing peat in a slurry to provide energy for the wet carbonization reaction (Cederquist and Bering, 1952). The aqueous slurry was preheated by indirect low temperature heat recovery from the filtrates, then brought closer to the reactor temperature by direct steam injection. A portion of the peat was oxidized in the wet combustion reactor, generating sufficient heat for the process. The remaining solids could be dewatered mechanically to $\sim$ 50% moisture and further dried by waste heat to 10-40% moisture.

The same process concept is one of those investigated in the present work.

Cederquist's work included laboratory autoclave and continuous flow pilot plant investigations. The capacity of the pilot plant was not given. The pilot reactor was provided with "an efficient horizontal agitator", but it was not further described. Only sketchy details of the reaction kinetics were provided, and these indicate a reactor mass throughput of 150 kg/hr-m^3 at a reactor temperature rise of 59°C. Feed concentrations were investigated in the range of 15-25% solids content.

A typical pilot plant material balance is given in Table 2.1. Unfortunately, the reaction conditions were not specified. From the data, it appears that 11.5% of the feed solids were solubilized and a further 17.1% were lost through oxidation and decarboxylation. A calculation of oxygen supply shows 14.5% of stoichiometric oxygen demand being provided, assuming 1.4 units of COD per unit of solids, with 1 unit of oxygen used to satisfy each unit of COD. Pure oxygen was injected into the reactor.

TABLE 2.1 - Material Balance in a Typical Pilot-Plant Experiment
Cederquist, 1952

Original dry substance in crude peat	158 kg	100%
Dry substance in solid product	113 kg	71.5%
Dry substance in solution	18 kg	11.4%
Reaction losses*	27 kg	17.1%
Net consumption of oxygen	22.5 m^3	
Specific combustion loss*	1.2 kg/m^3 O_2	

*Combined losses into gas phase due to oxidation and decarboxylation

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The heating value of the recovered solids was 5-10% above the moisture and ash-free heating value of the feed solids. The treatment did not materially change the ash content of the peat.

The solid product yield varied with the feed peat concentration, increasing from 73% at 15% feed to about 82% at 25% feed solids concentration. This appeared to be due to the decreasing trend in the extent of solubilization with increasing solids concentration. Unfortunately, the method of pumping such high concentrations of peat solids was not described.

Although the report is marred by the incomplete reporting of experimental conditions, a thorough mathematical treatment of dewatering through pressure filtration (up to 1 MPa) and pressing (up to 8 MPa) is provided.

In a later paper, Cederquist (1955) published additional data on the partial and complete wet oxidation of peat, performed in a laboratory autoclave (Table 2.2). Although the results were given without much commentary, certain trends were evident:

1. For complete oxidation, about 1.27 kg O_2 is consumed per kilogram of m.a.f. solids.
2. Above 195°C, complete utilization of oxygen occurs, at $\leq$ 10 minutes reaction time.
3. Even at partial stoichiometric oxygen supply, rather complete utilization of oxygen occurs.
4. Complete combustion occurs in the presence of adequate oxygen even at 31% solids suspension. In this case, the ash material was thought to catalyze combustion.

The idea of supplying process heat to the wet carbonization reaction through partial oxidation of the peat was also proposed by Chornet et al (1981) in his experimental study of a short residence time wet carbonization reactor. However, no experiments were performed to verify the concept.

TABLE 2.2 - Wet Combustion of Peat with Air - Cederquist, 1955

Feed Material		Oxygen		Reaction		Solubilization % feed solids
Solids %	Ash %	Conversion %	Supply kg O_2/kg m.a.f.	Temperature °C	Time minutes	
6.1	5.0	-	-	225	10	14
6.1	5.0	99.0	0.169	225	10	9
6.1	5.0	98.2	0.318	225	10	7
5.9	5.0	99.0	0.507	225	10	8
6.1	5.0	99.1	0.643	225	10	9
6.1	5.0	98.1	0.802	225	10	10
6.1	5.0	87.7	1.27	225	10	8
6.1	5.0	-	-	195	10	16
6.1	5.0	99.0	0.229	195	10	13
5.9	5.0	96.9	0.495	195	10	12
6.1	5.0	93.5	0.762	195	10	11
6.1	5.0	74.0	1.103	195	10	10.5
6.1	5.0	97.4	0.506	195	1	12
26.9	5.0	57.2	0.861	180	10	2
21.0	20.0	99.0	0.475	195	10	10

Contd.....

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TABLE 2.2 (Contd.)

Feed Material		Oxygen		Reaction		Solubilization % feed solids
Solids %	Ash %	Conversion %	Supply kg O_2/kg m.a.f.	Temperature °C	Time minutes	
31.0	20.0	71.0	1.27	195	10	3
31.0	20.0	71.4	1.27	195	30	4
31.0	20.0	70.1	1.25	195	60	2
31.0	20.0	74.7	1.33	225	10	2
31.0	20.0	46.9	1.11	185	10	N.A.

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Myreen, developer of the JP-Energy wet carbonization process, also investigated partial oxidation of peat in the course of wet carbonization. He found that the extent of solubilization occurring in the presence of oxygen was too great, leading to uneconomically high losses of recoverable peat solids (personal communication). No data were published on this aspect of the development work.

Apart from a few experiments performed by Cederquist (1955), total wet oxidation of peat has not been described previously in the literature to the best of our knowledge. The U.S. Department of Energy has been sponsoring partial and total peat wet oxidation research at the Grand Forks Energy Technology Center, but the results have not yet been released for publication.

Othmer (1980), based on his experience with the Zimmerman wet oxidation process, speculated on the potential advantages of total wet oxidation of peat slurries for energy production. In his paper, which was not based on actual experiments, he took it for granted that nearly total combustion of the peat would occur.

Wet carbonization of peat is a process which is mentioned on several occasions in this work. This concept consists of heating a peat-water slurry in a closed reactor at about 200°C and 2.5 MPa pressure. The resulting chemical changes render the peat dewaterable to about 50% moisture by mechanical rather than thermal means. The heating value of the treated material is increased by 5 to 20% on a dry basis, due to the loss of oxygenated compounds into the gas phase. The wet carbonization reaction forms the basis of the Finnish JP-Energy process which is presently promoted for commercialization. It has been described in a previous report (Monenco 1981, Chapter 4). Laboratory work and previous commercial development efforts connected with wet carbonization have been thoroughly reviewed by Mensinger (1980).

Wet carbonization processes are distinct from partial wet oxidation, as there is no oxygen being injected into the reactor. Instead, the process relies on extensive heat recovery from the effluents, junk

wood and waste sludges for preheating and process heat. The nature of the feed slurry leads to difficulties in heat exchange, as it is viscous and prone to foul heat exchanger surfaces. To overcome these problems in commercial practice, Myreen patented two novel heat exchanger designs (Myreen 1980a, 1980b) which are incorporated into the JP-Energy process that he devised. Apart from the patent specifications describing the principles of operation, no performance data have been published about these heat exchangers.

2.3 Anaerobic Digestion of Peat

2.3.1 General

Since dilute (3-10% solids) peat slurries will be fed into wet oxidation plants, massive amounts of wastewater will have to be discharged. This wastewater will contain the unreacted portion of the peat, solubilized to a greater or lesser extent. The wastewater will be treated by a two-stage system, consisting of an anaerobic first stage and an aerobic second stage. It is envisioned that a significant amount of energy will be recovered from the anaerobic stage in the form of combustible methane gas.

Although no published information has appeared to date dealing with the treatment of peat wet-process wastewaters, the anaerobic stage is analogous with a number of experimental systems. These will be briefly reviewed here, with a summary of their operating principle.

Peat is a material of biological origin and, as such, contains a rich variety of organic compounds: polysaccharides, humic acids, lignins, lipids, etc., most of which can be converted by bacteria, fungi and yeasts to methane, carbon dioxide and other useful products. The common feature of all biological conversions is that they take place in dilute aqueous media (85-99% moisture), low temperatures (< 65°C) and at atmospheric pressure. However, bioconversions proceed much slower than chemical processes.

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The motivation for the development of biological processes for peat conversion is twofold: wet-mined material may be used without dewatering and the waste water produced is environmentally innocuous and may be directly returned to the bog.

In order to make the peat more palatable to microbes and thereby increase the rate and extent of conversion, pretreatments such as comminution and alkaline or thermal hydrolysis or partial oxidation may be necessary. Adequate supply of inorganic nitrogen (C/N < 15) and phosphorus (C/P < 75) must also be present.

Of the products that may be prepared by the many schemes proposed (Le Duy, 1980), methane is the most significant, considering both the amount of development effort expended and the prospect of economic viability.

In a typical biological gasification scheme, peat (or biomass) containing 90-95% water is added on a continuous or intermittent basis at a loading of up to 16 g volatile solids/L-day (1 lb/ft^3-day) and a retention time of up to 20 days. In a stirred reactor, (or digester), from which air is rigorously excluded, a mixed population of anaerobic bacteria effect the conversion of up to 50% of the organic carbon to a mixture of methane and carbon dioxide ($\sim$ 60/40 by volume). This is equivalent to a methane yield of 0.25 m^3/kg VS (4 scf/lb VS). The maximum theoretical methane yield is 0.52 m^3/kg VS, based on 0.56 kg total organic carbon per kg volatile solids, if all the organics are converted.

Minor amounts of hydrogen and hydrogen sulfide may also be formed. These are the same reactions that produce marsh-gas in peat bogs.

Anaerobic digestion technology has been in use for waste activated sludge treatment for about 100 years. Anaerobic digestion research and development is currently very active in the biomass conversion and waste treatment fields and it is reasonable to expect that new findings in these fields will quickly be applied to peat.

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The major research problems consist of increasing the extent of carbon to methane conversion, and reducing the digester residence time from up to 20 days to a few hours. All of the biological conversion technologies to be described below are still in their early development stages, but the projected energy balances and economic studies show advantages over thermal gasification methods. Therefore, vigorous development of these processes is continuing.

Four methane-producing biological processes will be discussed in this section:

- Alkaline oxidative pretreatment of peat slurry followed by anaerobic digestion, under investigation at Dynatech R/D Company, Cambridge, Mass.
- BIOTHERMGAS™, a process being developed at IGT, which combines anaerobic digestion and thermal gasification of the residue for the total conversion of wet peat.
- Vyrmethane™, a small-scale process which recovers methane generated in situ from recirculating bog-water.
- Wet oxidation of peat and its subsequent anaerobic treatment.

2.3.2 Biogasification of Peat (Dynatech R/D Company)

The Dynatech R/D Company has conducted extensive work on the conversion of Minnesota sedge peat to methane for use as a pipeline quality fuel. In their work (Buivid et al, 1980) they have investigated a broad range of alkali pretreatment and anaerobic fermentation conditions in an effort to enhance the conversion efficiency of peat to methane. Pretreatment conditions investigated included chemicals used ($Ca(OH)_2$, NaOH, K_2CO_3, Na_2CO_3), reaction concentration, temperature and duration and subsequent oxidation of alkali treated peat. Fermentation trials have been conducted in batch and continuous stirred tank reactors and under mesophilic and thermophilic conditions. Table 2.3 summarizes the effects of these variables on the conversion efficiency of peat to methane.

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TABLE 2.3 - Conversion of Peat to Methane
Dynatech R/D

Pretreatment Temperature[1]	25°C	25°C	100°C	115°C	150°C	150°C	150°C	170°C	200°C	200°C	200°C	200°C
Pretreatment Chemical[2]	none	none	NaOH	$Ca(OH)_2$	none	none	NaOH	K_2CO_3	none	NaOH	none	NaOH
Oxidation[3]	none	none	none	none	none	yes	yes	none	none	none	yes	yes
Fermentation Temperature[4]	60°C	35°C	35°C	35°C	35°C	35°C	35°C	35°C	35°C	35°C	35°C	35°C
Approximate Methane yield (m^3/kg volatile solids)	<0.01	0.015	0.07	0.02	0.043	0.09	0.18	0.06	0.08	0.13	0.07	0.15

[1] Reaction time was 20-30 min heat up, 1 hour at temperature and 20 min to cool

[2] Concentrations were selected to leave 100 meq/L after treatment

[3] Oxidation was performed at 1 MPa during pre-treatment

[4] Fermentations were carried in batch fermentors

Quoted from Buivid et al, 1980

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A preliminary plant design (Ruoff et al, 1980) was developed based, in part, upon the more favourable conditions determined in the experimental work. The process consists of the following steps:

(1) Raw peat is dewatered to 8% consistency.

(2) Peat solids are solubilized at 150°C in 2.4% Na_2CO_3 to produce 90% conversion of phenols from lignin and soluble sugars.

(3) Solubilized peat is subjected to partial wet oxidation at 150°C and 150 psi to oxidize 90% of lignin aliphatic side chains to carboxylic and aldehydic groups. Some of the energy produced in this step is recovered by heat exchange with the feed stream.

(4) Solids are separated by sedimentation and subsequently dewatered for use as fuel.

(5) The liquid portion is fermented in a continuous stirred vessel to convert 67% of the fermentable products to methane (60%) and carbon dioxide (40%).

The scheme entails a methane yield of 0.28 m^3/kg volatile peat solids. An economic analysis of an 8000 dry tonne of peat per day biogasification facility was carried out using literature values for capital costs. The analysis predicted a product gas cost of $7.53/GJ. The projected capital cost was $291.7 million and the annual operating cost was estimated at $138.6 million. It should be noted that these costs were derived using a dry peat cost of $3.98/tonne. If a cost of $18.70 dry tonne of wet-mined Canadian peat is employed (note Section 3.4), the unit gas cost is increased by $1.87/GJ.

2.3.3 Anaerobic Digestion and BIOTHERMGAS™

Workers at the Institute of Gas Technology (IGT) have also conducted extensive trials on the fermentability of Minnesota sedge peat to methane (Ghosh and Klass, 1979). They investigated the influence of several variables including peat particle size, acid and alkali

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pretreatment and fermentation temperature. These trials were conducted in small scale batch thermophilic fermentors. The results of this work are summarized in Table 2.4. The authors concluded from the study that the combination of particle size reduction and alkali pretreatment could produce a methane yield approaching 60% of that which is theoretically possible.

The IGT group has proposed a novel process, called BIOTHERMGAS^{TM}, for extending the yield of fuel gas from wet feedstocks. While experimental and economic investigations have centred upon biomass (Chynoweth et al, 1980), e.g., Bermuda grass, the process is thought to be applicable to wet-mined peat.

The key aspects of the process are the thermochemical conversion of non-fermentable peat solids to hydrogen and carbon monoxide and subsequent conversion of these gases to methane. The methanation process is to be accomplished by chemical catalysis or by biomethanation in the anaerobic fermentors. Preliminary plant designs have been developed for the process, which predict methane yields of 0.36 m^3/kg volatile solids. The economics of methane production from a 10,000 tonne per day facility have been predicted at $6.10/GJ. The capital costs were projected to be $492 million.

2.3.4 Vyrmethane^{TM}

Vyrmetoder AB of Sweden has developed a process called Vyrmethane for the production of methane directly from peat bogs (Martinell, 1981). The process involves the collection of bog water from shallow wells, its vacuum degassing to remove methane and carbon dioxide and its subsequent return to the bog via parallel recharging wells. Successful operation of the process is understood to require a minimum hydraulic permeability of 10^{-5} m/s and a degree of humification below H5. 241 m^3 of methane/day has been predicted for a 25 ha bog area with a mean annual temperature above 6°C. The process employs 25 ha modules, each complete with piping, pumps (at 100 L/s), degassing equipment and gas

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TABLE 2.4 - Conversion of Peat to Methane
Institute of Gas Technology

Pretreatment	none	none	none	none	8% HCl 132°C, 193 KPa	3% NaOH 132°C, 193 KPa
Particle Size	as received	fine	fine	coarse	fine	fine
Fermentation Temperature	55°C	55°C	65°C	55°C	55°C	55°C
Approximate Methane yield* (m^3/kg volatile solids)	0.012	0.034	0.018	0.017	0.037	0.041

*Assuming 60% methane content of gas evolved

Quoted from Ghosh and Klass, 1979

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powered generators to meet process requirements. 65% of the methane produced is in excess of the process needs.

The typical capital cost of a 25 ha module is claimed to be $37,000 (exclusive of land costs), with an annual operating cost of $11,225 and resulting in a methane cost of $5.98/GJ (1981 costs).

2.3.5 Peat Enhancement by Wet Oxidation

Preliminary work has been conducted at the Michigan Technological University (Bettinger, 1982) on the total and partial wet oxidation of native peat. Total oxidation trials determined a maximum level of peat combustion under conditions of between 260 and 290°C and 4.8 to 6.9 MPa. These rigorous conditions were not considered to be economically viable for energy (i.e. electricity) production.

Partial wet oxidation and wet carbonization of peat at 190°C over 10 minutes was employed to improve the filterability of the peat. Partial wet oxidation resulted in 13% combustion of carbon and greatly enhanced filterability. Filtrate from both wet oxidation and wet carbonization were rich in COD and subsequently determined to be 87% reduced in respirometer trials.

Small scale anaerobic fermentation trials were conducted in mixed vessels at 35°C. After some initial difficulties, a 36.6% soluble COD removal efficiency was noted. Gas composition was 82% methane and amounted to 0.236 m^3/kg volatile solids applied to the fermentors. In terms of the raw peat before partial oxidation, the methane production was approximately 0.023 m^3/kg peat volatile solids.

3. TASK 1 - WET MINING OF PEAT

The recognized advantages of the wet mining of peat notwithstanding, there are few such operations known and cost information about them is even more scarce. This state of affairs is attributable to the lack of large-scale, economical methods of peat dewatering. As wet oxidation, wet carbonization and biogas digestion processes approach commercialization, the study and evaluation of wet mining techniques will have to proceed along with downstream process development.

3.1 Wet Mining Methods

Wet mining methods, which utilize hydraulic or mechanical excavators for one pass removal of peat require little site preparation. Trees and brush may have to be removed from the bog surface. However, extensive draining and grading of the production areas is not required because harvesting machinery does not travel on the top of the peat. Instead, high pressure water monitors or floating dredges are used to excavate the peat, which is then pumped as a slurry to a dewatering area.

Wet peat harvesting methods are subdivided into:

- slurry pond method
- slurry ditch method
- hydro peat method

Information on these harvesting methods is limited because they have not been frequently used. Historically, small scale hydraulic operations were sometimes successful in regions where dry harvesting methods were not technically feasible due to adverse climatic conditions or poor terrain for drainage.

3.1.1 Slurry Pond

In this method, mechanical excavators or dredges are employed to cut the peat in a central pond within a bog. The peat slurry is recovered by a pump and transported through pipelines to the processing area. Three types of equipment can be utilized:

(a) The grapple dredge - It is most commonly a clamshell-equipped derrick mounted on a suitable hull. Peat is excavated with the clamshell, dumped into ditches or swamps where the peat material is broken up and separated from roots and stumps by high pressure water jets and then pumped as a thin slurry to the dewatering area. The derrick-clamshell arrangement may be replaced with a backhoe or dragline. For example, Fisons-Western Peat Corporation operate a barge mounted hydraulic backhoe with a clamshell bucket near Vancouver, B.C. Similarly, a float-mounted dragline is used to excavate peat at a commercial peat operation in Florida.

(b) The cutter-suction hydraulic dredge - The cutter head dredge consists of a many-bladed cutter head rotating at the end of a heavy structural steel frame (called the ladder) hinged horizontally to the bow of a suitable hull. The outer end of the ladder is raised or lowered by a wire rope from a derrick at the front of the boat. The ladder also contains the suction pipe and the necessary drive gear for the cutter head. In place, peat is cut up by the cutter head, sucked into the suction pipe and pumped to the processing area. The dredge is manoeuvered using a spud swing anchor or a spud-push-spud system. G. B. Morris (1982) has recently published a study of dredging technology and costs as applied to peat production. This paper will be reviewed later as a case study.

Several examples of peat dredging operations have been reported (Gas Research Institute, 1980). A recently completed study of peat dredging costs (W. Hudak, 1982) on behalf of the Gas Research Institute will be reviewed later.

The U.S. Peat Corporation in South Carolina produced horticultural grade peat in the 1970s using a 10" cutter suction Dixie dredge and later, a modified 8" Mudcat dredge. The peat slurry, which contained less than 5% solids by weight, was pumped from the dredge into ditches, where the peat was allowed to settle out. A dragline dug the peat from the bottom of the ditches and spread the peat on the ground for

drying. Production capacity was estimated to be approximately 40 cubic yards per hour for the 8" dredge and 75 cubic yards per hour for the 10" dredge.

The Markman Peat Company is presently excavating peat with the same system, except that an 8" Kenna Marine dredge is used. Production is estimated to average about 100 cubic yards per hour. No costs are available for either of these operations.

Morris considers 16" to be the minimum size for cutter heads; in his opinion, smaller sizes would be inadequate for macerating the woody material in the bog. It would be interesting to find out if this assumption is correct in the light of the operating experience of smaller dredges in the U.S.

(c) Ladder dredge - The ladder dredge has a series of buckets rotating around tumblers or drums at each end of the ladder. Material is scooped up by the buckets and then dumped into chutes or conveyors when the loaded buckets rotate over the top tumbler. The material is then usually dumped into barges alongside or conveyed by belt to the desired area. The material is also sometimes dumped into hoppers, slurried and pumped.

It is not known if ladder dredges are presently harvesting peat. They are closely related to the bagger, which is used in sod peat production in Ireland and Germany.

According to Mohr (1976), the ladder dredge has several important advantages over other dredging methods, which could make it most suitable for peat production:

- The power required to operate a ladder dredge is approximately one half of that required for a suction cutter head dredge.
- Ladder dredges do not dilute and grade material like hydraulic dredges. A mechanical dredge handles material with almost in-place density, whereas hydraulic dredges dilute material by up to several hundred percent.

- Ladder dredged material can be conveyed directly from the barge to the dewatering area. Belt conveyors are commonly used in Europe for dredged material. Conveyor sections are floated on pontoons and are more flexible than floating pipe with ball joints.
- Ladder dredges, using conveyor or barge haulage, are more adaptable to long distance transport than hydraulic dredges.

3.1.2 Slurry Ditch Method

In this system, high pressure water monitors cut the peat from the face wall of a ditch. The peat drains away from the face, while roots and debris remain. The peat slurry is recovered by a submerged pump and pipelined to the processing area. The slurry ditch system is the oldest hydraulic production method and, historically, the system was used on a small scale in Europe. Today, it is not commonly used because it is not efficient for achieving high production rates (Monenco, 1978).

3.1.3 Hydro Peat Method

This system combines the slurry ditch and sod peat systems. High pressure water monitors cut the peat from the face wall of a ditch, and the resultant slurry is pumped to a drying field for air drying. The slurry is spread over the ground and a peat cake is formed. After several days of drying, the peat cake is cut into sods to accelerate drying. After additional days of drying, the sods are transported from the drying fields using either truck or rail systems.

Historically, the hydro peat system was used in Denmark and the U.S.S.R. on bogs where other production methods were not suitable. In Denmark, peat slurry containing about 4% solids was produced at a rate of about 200 m^3/hour (Monenco, 1978). In the U.S.S.R. in the 1950s, 600,000 tpy of 5 % moisture peat were produced from the Vasilienski-Mokh bog using this system. The hydro peat system has been replaced by milled

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peat operations, because power and labour costs were high, equipment needs were high and the efficiency of peat recovery was low.

According to Mr. K. Leppa of Ekono Ltd., the hydro peat method may be revived for a fuel peat mining operation now under study in Burundi, Africa. The intense solar radiation available at the site may allow economical drying in that special situation.

3.2 Wet Mining Costs

Since hydraulic mining of peat is practised only at a few locations, cost information is very scarce. Only four items of information were discovered: mining costs at Fisons-Western Peat Ltd., Vancouver operation, reported by the Gas Research Institute (1980); mining and truck transportation costs at a peat mine in Polk County, Fla. (J. A. Fraser, Monenco Ltd., personal communication); the recently completed "Study of the Technology and Costs ... for the Recovery of Peat" by G. B. Morris (1982); and a yet unpublished report by Dravo Corp to the Gas Research Institute.

Hydraulic mining costs cannot be presented for a generalized operation. The quantity of peat produced, the pumping distance and operation layout and the solids content in the production slurry must be known before a realistic cost may be estimated.

3.2.1 Fisons-Western Peat Ltd.

The British Columbia division of Fisons-Western Peat Ltd. was visited by representatives of Dravo Corporation, IGT and Williams Bros. Engineering on May 20, 1980. The following is a summary of their report, published by the Gas Research Institute (1980).

Peat reserves at the Vancouver operation total about 7,480 ha and about 60 ha are depleted each year. The bog is primarily Sphagnum moss, ranking about H3-4 on the Von Post scale. The peat contains an unusually large amount of woody material. The bog thickness is usually over 2.5 metres. All of the peat produced is sold for horticultural use. Annual production is 28,000 tonnes/year at 55% MC.

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About 68-75 m^3 of peat bog are excavated per hour with a backhoe equipped with a 3/4 yd^3 clamshell bucket. The backhoe is mounted on top of a hover barge, which floats in the depleted area of the bog. The backhoe dumps the peat into a hopper (also located on the hover barge) where water monitors break up and wash the peat from woody material. The roots and wood pieces are pulled out of the hopper by rotating combs and are dumped overboard. The peat washed from the hopper drains into a holding tank and is pumped as an 0.9 to 1.4% solids by weight slurry to the dewatering plant 4.2 km away. The barge and pumps are powered by diesel engines.

Total harvesting and pumping cost was given as $68.80 per dry tonne (U.S.$, 1980). The report from which the above is quoted gives a detailed breakdown of mining and drying costs.

3.2.2 Monenco Ltd.

The wet mining costs reported by Monenco (1981) were derived from a visit by Monenco personnel to a peat mining operation in Polk County, Florida.

The peat was excavated by draglines mounted on floating pads. The bog was drained previously; therefore, the peat could be extracted at 15% solids content, loaded into trucks and transported to the storage site. The mining cost, including bog preparation, but without transportation, was C$3.80 per tonne, at 85% moisture content. This is equivalent to C$25.33 per dry tonne. This figure is based on 200,000 dry tonnes/year scale, where four excavators are operating 39 weeks/year.

Truck transportation costs were also calculated, based on 15 km average haulage distance and 39 weeks' mining season. Additional assumptions are shown in Table 3.1. Trucking costs were C$6.67 per dry tonne.

TABLE 3.1 - Assumptions for Wet Mined Peat Haulage Costs

Average Distance	15 km
Quantity, at 85% MC	1.34×10^6 tonnes
Haul Schedule	390 shifts/yr
Truck Capacity	35 wet tonnes
Trucks Required	8
Owner-operator Rate	$45/hour
Contingency	20%

3.2.3 Kesmark Ltd.

G. B. Morris (1982) of Kesmark Ltd. published a report, in which he applied his experience with cutter-suction dredging of overburden to peat mining with this equipment. Since the costs of dykes and the water recirculation system depend on the bog topography and the water content of the bog strongly influences the production costs, each mine site must be evaluated individually. Therefore,he presented three case studies for evaluation:

- the Meinzinger bog in Northwestern Ontario
- the Onakawana area in the Hudson Bay lowlands
- a marsh in Southern Ontario.

All three areas had peat deposits exceeding 2 meters in thickness, railroad access and adequate water for floating the barge on the slurry pond.

He observed that peat could be mined at 7-8% solids content, although this would have to be confirmed by actual tests. Homogenized fuel peat slurries certainly appear to be pumpable up to 10% solids content according to our own experience in the pilot plant. On the other hand, Vanasse et al (1979) found that moss peat of low degree of humification (e.g. horticultural grade) would be difficult to pump above 3.5% solids content.

It is suggested in the Kesmark report that peat dredge design would have to be modified from the usual equipment and these changes would have to be tested in practice, especially those involving the cutterhead. However, existing dredges already produce peat in the U.S., although there are no details of their operating experience.

Rather massive scales of dredging operations are envisaged in Morris' study. In his opinion, the minimum dredge size would employ a 16" cutterhead, a smaller unit would be unable to cut through tree trunks and roots found in many bogs. He may be too conservative in this estimate, since there are peat dredging operations on record which use cutterheads as small as 8" in diameter. The production rate

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calculated for the 16" dredge is 0.67 x 10^6 tonnes/yr dry peat, assuming around-the-clock operations, nine months of the year. The installation consuming such a production would have a thermal capacity in the order of 300 MW.

The costs developed for the three case studies are given in Table 3.2.

3.2.4 Dravo Corporation

In the course of a discussion, Mr. W. Hudak of Dravo Corporation, Pittsburgh, PA., disclosed the results of a study prepared for the Gas Research Institute. In this study, peat would be mined by cutter-suction dredges in Northern Minnesota to support the operation of a 250 x 10^9 Btu/day SNG gasification plant. This would require the removal and delivery of 8.52 x 10^6 dry tonnes of peat per year over an eight-month production season.

A detailed feasibility study estimate was prepared. Some of the underlying assumptions are given in Table 3.3. Bog preparation work included clearing the surface to the grass roots, clipping the woody materials and leaving it on the bog to be mixed with the peat and separated at the dewatering facility. No bog draining was included and the topography of the site allowed open channel return flow by gravity.

Dravo engineers reviewed the literature dealing with slurry transport and developed equations for pressure drops in peat slurry pumping. Their conclusion was that unhomogenized peat slurry pumping was not economical above 3% solids concentration. In their trial design for 3% slurries, they used 14 ft/sec flow velocity in 48" steel pipes with a head loss of 3.9 ft/100 ft. Average transport distance over the lifetime of the project was 10 miles.

TABLE 3.2 - Comparison of Costs of the Three Ontario Peat Deposits Covered

(from G. B. Morris, 1982)

	Western	Hudson Bay Lowlands (A floating plant)	Southern
Dredge size	24 inch	24 inch	16 inch
Dredging season	9 months	8 months	9 months
Peat depth dredged	2 meters	5 meters	2 meters
Annual production dry peat (tonnes)	1.5×10^6	1.4×10^6	0.67×10^6
Horsepower - Dredge on board Booster pump	2,300 1,300	2,800 -	1,350 3,300
Pipeline max. length	7 km	4 km	15 km
Capital Cost - Dredge Booster pump	$4,160,000 $600,000	$4,260,000 -	$2,300,000 $2,000,000
Auxiliary equipment	$2,250,000	$2,200,000	$1,530,000
Annual crew cost	$1,725,000	$1,750,000	$985,000
Dykes, diversions, dams, roads (over 20 years)	$27,000,000	$6,410,000	(Chargeable to land development)
Dredge - Capital & Operating Cost (including dykes) per dry tonne peat	$3.01	$2.39	$3.16
Omitted Cost - per dry tonne	$1.51*	$0.91*	$1.23**
Total Cost - per dry tonne of peat	$4.52	$3.30	$4.39
Subsequent land use	Biomass	Forestry	Market gardening

* Cost of surge capacity, interest at 15% p.a. sinking fund, project engineering, 20 c/tonne royalty

**Dykes and river diversion for land reclamation

TABLE 3.3 - Design Assumptions: Wet Mining of Peat
Dravo Corporation

Scale of operations	8.52×10^6 dry tonnes/year
Life cycle	20 years
Dredges	Seven, Ellicott Series 500 36" cutter suction
Fuel	Dredges and pumps electric
Electricity cost	6¢ U.S./kWhr, incl. transmission line
Financial assumptions	75/25 debt to equity 9% interest on debt 15% ROE after 48% tax
Pumping distance	10 miles average
Work force	6-700 employees

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Levelized production costs over 20 years were:

1% solids slurry	U.S. $25.30/dry tonne
2% solids slurry	U.S. $15.40/dry tonne
3% solids slurry	U.S. $18.70/dry tonne

Transportation of the slurry is a major cost factor. Therefore, at half the production rate (shorter pumping distance), the production cost was found to decrease to $12.10/dry tonne at 2% solids. When the report is published and detailed cost factors are known, price sensitivity to other production scales and parameters may be calculated.

3.2.5 Summary of Wet Mining Costs

Although the wet mining costs reported for Fisons-Western Peat Ltd. are the best documented, they cannot be used for the evaluation of a fuel peat mine. Horticultural peat is a high-value product and the conomic pressures to minimize production costs are not as severe as in the case of fuel peat mining.

The costs reported by Monenco Ltd. for the Florida operation appear to be applicable for annual production capacities of 50,000 dry tonnes and up. Four excavators are used for an annual capacity of 200,000 tonnes/year and no economies of scale are apparent. Therefore, the mining cost of $25.33/dry tonne will be used for applications covering this production range. The delivered moisture content is 85% in these cases. Transportation costs, in this case, also appear to be insensitive to scale of operation, and will be assumed at $6.67/dry tonne for material delivered at 85% moisture content.

For large scale operations, dredging and slurry pumping must be applied. Pumping of unhomogenized peat slurries above 3% solids is probably impractical. Therefore, homogenization must occur at bogside, or even aboard the dredge, before the slurry enters the pipeline. The pumping characteristics of homogenized peat are not known. The dredging costs per dry tonne of peat (as far as they are known) are inversely proportional to the moisture content of the excavated peat.

Pumping cost is a variable portion of the total production cost, depending upon slurry concentration, rheology and pumping distance.

Since the detailed evaluation of wet mining costs is beyond the scope of this study, it will be assumed that it will be available at the processing plant for C$5 per dry tonne at the annual production volume of 670,000 dry tonnes.

The mined peat costs encountered in the literature ranged from $0.253 to $4.80 per wet tonne at solids concentrations of 1 to 15% respectively (Table 8.1). The cost most likely to reflect reality at the scale of processing evaluated in this study is $4.80 per wet tonne, delivered by truck at 15% solids content.

The economic evaluation of wet oxidation processes which follows in Section 8 will vary the feed peat cost and solids concentration over the range encountered in wet mining studies to date. There will be sufficient product and capital cost data generated to estimate costs for the conditions that will be generated in future wet mining case studies.

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4. TASK 2 - TOTAL WET OXIDATION OF PEAT

4.1 General

The process concept explored by these experiments is aimed at wet combustion of peat slurry to the maximum extent practicable, and recovery of the energy liberated in the form of heat or electrical energy.

In these experiments, the extent and velocity of the reaction is investigated, in the presence of excess oxygen for a variety of conditions. A simple, three parameter kinetic model will be proposed and its applicability confirmed in continuous flow, scaled-up experiments. The effects of peat characteristics and metal catalysts on the kinetics will also be investigated. The results of corrosion tests will also be reported here.

4.2 Experimental

4.2.1 Description of Peat Samples

Several tonnes of fuel-grade peat have been obtained for the experimental programme from three Canadian locations. One sample was excavated from Western Peat Moss Ltd., Elma bog, 100 km east of Winnipeg. Another sample was dug from the Trewartha bog in Northwestern Ontario, about 140 km northwest of Thunder Bay. The third sample was obtained from Noval Technologies Ltd. from their production scale bogs in Newfoundland. All samples were collected and shipped with the associated bog-water.

Table 4.1 compares the relevant characteristics of the three peat samples. The Manitoba and Northern Ontario samples were highly decomposed (H9), whereas the Newfoundland sample was of medium degree of decomposition (H5-6).

According to botanical origin, the Manitoba peat was classified as Carex-Sphagnum with some fine roots present; the Northern Ontario peat as Sphagnum with a small amount of well decomposed woody material, whereas the Newfoundland peat was wood-sedge peat with a considerable amount of shrubby residues.

TABLE 4.1 - Peat Characteristics

Origin	Manitoba	Northern Ontario	Newfoundland
Humification (Von Post)	H8-9	H8-9	H5-6
Botanical Origin	Sphagnum-Carex	Sphagnum	Wood-sedge
Moisture (%)	94-96	81-84	91.8
*Ash (%)	8.2	10.8	11.2
*Sulphur (%)	1.2	0.3	0.26
*TKN (%)	2	1.7	1.9
COD (%)	6-9	24-27	10.4
*Heating Value (Btu/lb)	8410	8900	8500
Heating Value (Btu/lb COD)	5920	6140	6690
Heating Value (MJ/kg)	19.5	20.7	19.7
Heating Value (MJ/Kg COD)	13.7	14.3	15.5

*Based on dry weight

4.2.2 Preparation of Peat Samples

A small amount of hard woody material was removed by hand from the peat samples. Soft, decomposed roots, etc., were blended in with the total sample. The small valve, etc., clearances in the laboratory and pilot plant apparatus necessitated maceration of the peat. Although the peat particle size may influence combustion kinetics, it is expected that, on production scale as well, the peat would be disintegrated in order to provide a pumpable slurry.

For bench scale experiments, the peat was treated in a 1-gallon size Waring Commercial Blender, Model CB-6, for 5 minutes. In the pilot plant, the contents of the feed-tank were diluted 1:1 by water and the slurry was continuously recirculated a 19 L/min using a 1/2 H.P. Robbins-Myers pump (Model WA 150CGQ) which contains a cutterhead disk ahead of its progressing-cavity pumping section.

Samples prepared by either method were examined under a Quantimet 720 Image Analyzing Computer to arrive at a particle size distribution.

Automatic sizing could not be carried out, since most of the particles were near-colloidal size ($\sim$ 0.5 - 1 μm) and exhibited Brownian motion. Upon drying, the particles agglomerated and would not redisperse suspended in a hydrocarbon liquid.

A visual comparison of the Waring Blender and macerator-pump treated samples under the microscope showed that the former contained a higher proportion of fibre-like material and the latter sample appeared to have a higher proportion of very large ($\sim$ 50 μm) particles. No quantitative evaluation was possible.

4.2.3 Analytical Methods

The main reference texts used as the source of analytical methods were: "Standard Methods for the Examination of Water and Wastewater", 15th edition, 1980 (abbreviated SM) and "Annual Book of ASTM Standards, Part 31" (abbreviated ASTM).

Ammonia - Distillation of wet sample in NH_3 free water buffered to pH 9.5. Determination of ammonia in distillate by Nesslerization. Reference: SM Method No. 417A, B.

Biochemical Oxygen Demand (BOD - Empirical test measuring oxygen demand produced by carbonaceous and nitrogenous compounds using settled fresh domestic raw sewage as seed. Measurement of initial dissolved oxygen in the sample and dissolved oxygen remaining after five or ten days of incubation at 20°C by acid modification of iodometric titration. Reference: SM Method No. 507, 421B.

Chemical Oxygen Demand (COD) - Reflux sample in a sealed tube with $K_2Cr_2O_7$ and Ag_2SO_4 and $HgSO_4$ catalyst. Spectrophotometric measurement of the increase in CrIII. Reference: Knechtel, 1978.

Soluble Chemical Oxygen Demand (SCOD) - COD determined after filtration of sample through glass fibre filter disks, which were previously ignited at 550°C.

Total Kjeldahl Nitrogen (TKN) - Micro-Kjeldahl digestion of wet sample with H_2SO_4, K_2SO_4 and $HgSO_4$ solution, followed by micro-scale distillation into boric acid solution after making digestate alkaline with NaOH-$Na_2S_2O_3$reagent. Reference: ASTM Method No. D 3590-77.

Total Phosphorus (TP) - Mild acid hydrolysis of wet sample with H_2SO_4-HNO_3 solution. The test will determine condensed phosphates, polyphosphates, orthophosphate and organic phosphates which are converted to orthophosphate under the conditions of the test. After hydrolysis, orthophosphate is determined by stannous chloride-ammonium molybdate colorimetry. Reference: SM Method No. 424B, E.

Total Solids and % Moisture (TS & %MC) - Volumetric or gravimetric measurement of initial sample, evaporation at 103-105°C and gravimetric measurement of dry residue. Reference: SM Method No. 209A, G.

Fixed and Volatile Matter (Ash, VS) - Ignition of residue obtained in TS test at 550°C for one hour. Gravimetric measurement of ash.

Total and Volatile Non-filterable Residue (SS and VSS) - Filtration of sample through glass fibre disks, previously washed and fired at 550°C. Suspended solids are dried at 103-105°C, followed by gravimetric measurement of solids retained by the filter. Ignition of suspended solids at 550°C for one hour and gravimetric measurement of loss of residue. Reference: SM Method No. 209D, G.

Volatile Acids (VA) - Digestion and steam distillation of the sample in the presence of H_2SO_4. The distillate is titrated with NaOH. Reference: SM Method No. 504C.

Heating Value - The sample is combusted with gaseous oxygen in a Parr calorimeter and the fuel value is calculated from the resulting temperature rise. Reference: ASTM Method D240-76.

Sulphur Content - The sample is combusted with gaseous oxygen in a Parr bomb and the resulting ash is taken up in bromine water. The resulting sulfates are determined gravimetrically with $BaSO_4$.

Trace Elements - The samples were ashed at 550°C. The ash was extracted with aqua regia, filtered and an aliquot analyzed by a DCP Atomic Emission Spectrophotometer.

4.2.4 Equipment and Technique

4.2.4.1 Batch Autoclave

Batch experiments of partial and total wet oxidation were carried out in a 2-litre stirred autoclave. The autoclave is constructed of titanium and it can withstand pressures up to 13.8 MPa (2,000 psia). Temperature control was accomplished by means of external electrical heating coils for preheating and an internal cooling coil to remove heat from the combustion reactions. The internal reactor temperature was measured by a thermocouple which was connected to a continuous chart recorder.

The reactor was stirred at 800 RPM by two six-bladed turbine impellers mounted on a single shaft.

The layout of the autoclave installation is shown schematically in Figure 4.1. The sample injection system was used only with the total oxidation experiments.

The batch kinetics of the wet combustion of peat were studied at several reaction temperatures ranging between 171°C to 271°C. As it was determined that oxygen coneentration did not influence the reaction rate, adequate oxygen partial pressure was provided above the vapour pressure of water to give an oxygen/COD stoichiometric ratio of at least 3:1 and higher. The peat sample was injected into the preheated autoclave by pressurized oxygen.

The reactor was initially charged with 750 mL of water, sealed and heated to obtain an internal temperature ∿ 28°C above the desired reaction temperature. A 50 mL sample of homogenized peat was placed into the sample injector cylinder, together with 100 mL of water. 50 mL flushing water was placed into the wash-water cylinder. When the appropriate temperature was reached, pressurized oxygen was used to inject the sample, followed by the wash-water. This was taken as time zero.

The injection of cold liquid immediately dropped the temperature of the reactor down to the desired reaction temperature. Once the peat began to burn, within a few seconds, the correct reaction temperature was maintained by the manual adjustment of cooling water flow.

Oxygen dose was adjusted by bringing the total pressure in the reactor to a predetermined value at the reaction temperature.

Samples were withdrawn from the reactor at 3, 6, 10, 20, 40 and 60 minutes, following the injection of peat. They were analyzed for chemical oxygen demand to characterize the reaction kinetics.

Known quantities of peat slurry were placed in the injection system with the usual amount of flushing water inside the wash-water cylinder. The sample was injected into a cold, pressurized autoclave and the COD concentration in the autoclave was subsequently measured. Five repeated experiments showed that, on the average, 93% of the COD

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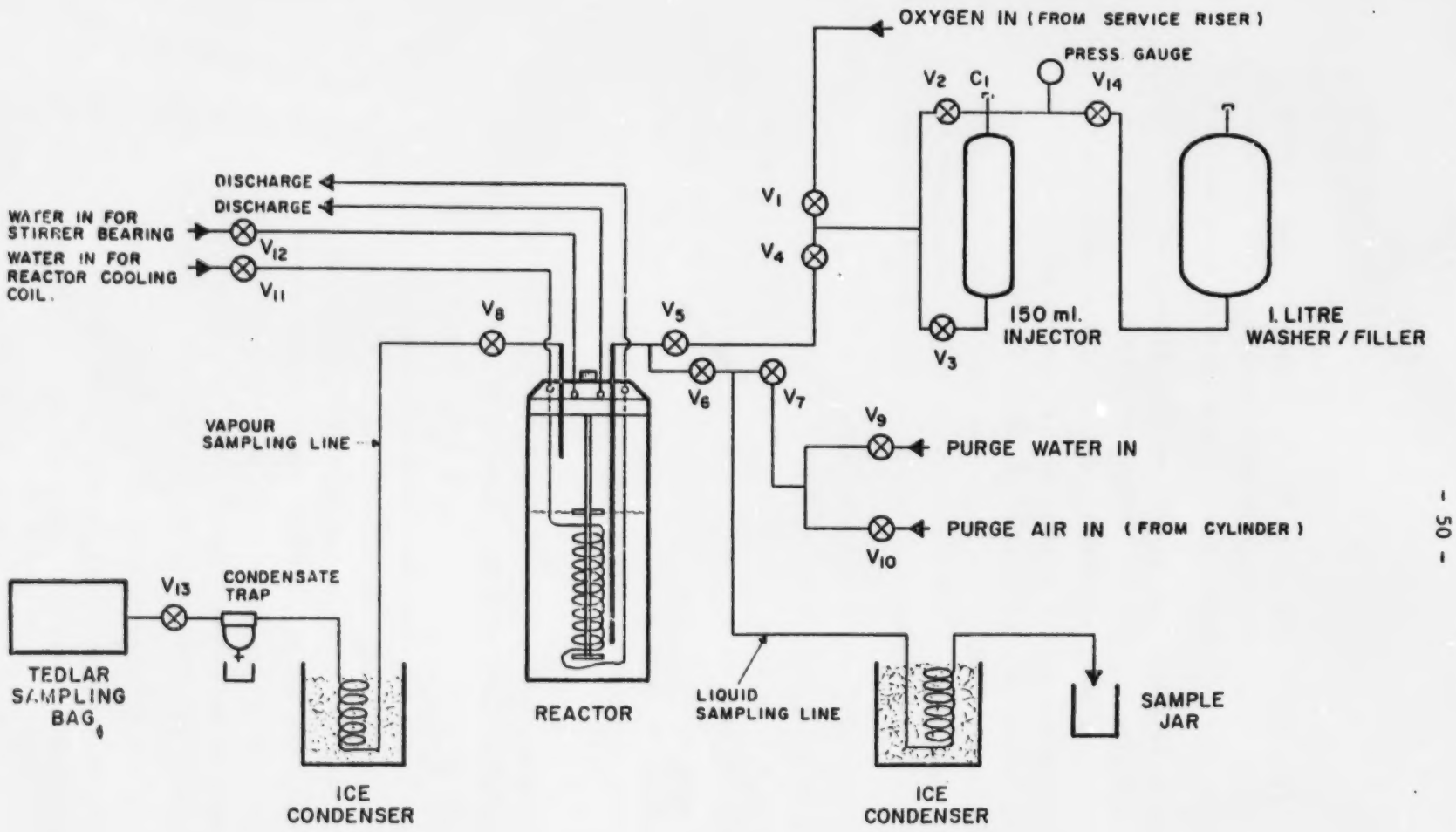

SCHEMATIC LAYOUT FOR 2-LITRE AUTOCLAVE.

FIGURE 4.1

measured into the sample cylinder is actually transferred into the autoclave under simulated experimental conditions. Therefore, the COD starting concentrations were routinely reduced by this value.

The precision of the COD test is considered to be $\pm$ 6.5% (Water Pollution Control Federation, 1980). The effect of this on the value of K_1 is variable. At 50% conversion at 10 minutes time, the error in K_1 due to this is approximately 10%, appearing larger at the beginning and the end of the reaction. The reliability of the kinetic model (developed in Section 4.4.1.1) was estimated by comparing predicted and experimental values of COD reduction for a wide range of experimental conditions in batch and continuous flow experiments.

4.2.4.2 Continuous Flow Pilot Plant

The wet oxidation of Northern Ontario peat was tested using the Wetox(R) pilot plant operated with a continuous supply of both peat and air. The pilot plant provides realistic conditions for evaluating the process in a continuous mode of operation. Data from the pilot plant can be used to both test the validity of the batch kinetics and provide data for a preliminary economic assessment of a full-scale system.

The Wetox pilot plant consists of a four-compartment, 36-litre titanium reactor, heat exchangers, plus a variety of instrumentation and control systems (Figure 4.2).

The raw Northern Ontario peat feedstock was prepared according to the description in 4.2.2. The raw peat was atypically low in moisture and, therefore, high in COD concentration, about 81% and 24% respectively. This was a result of the manual excavation method which allowed the peat to be recovered without mixing with the surface water in the bog. During the maceration of the raw peat, measured quantities of water were added in order to produce a peat solution of various selected COD concentrations.

Once sufficient quantity of feed material had been prepared, usually about 180 litres, heat-up of the pilot plant was started. Before the wet oxidation reaction can occur, the organic material must be

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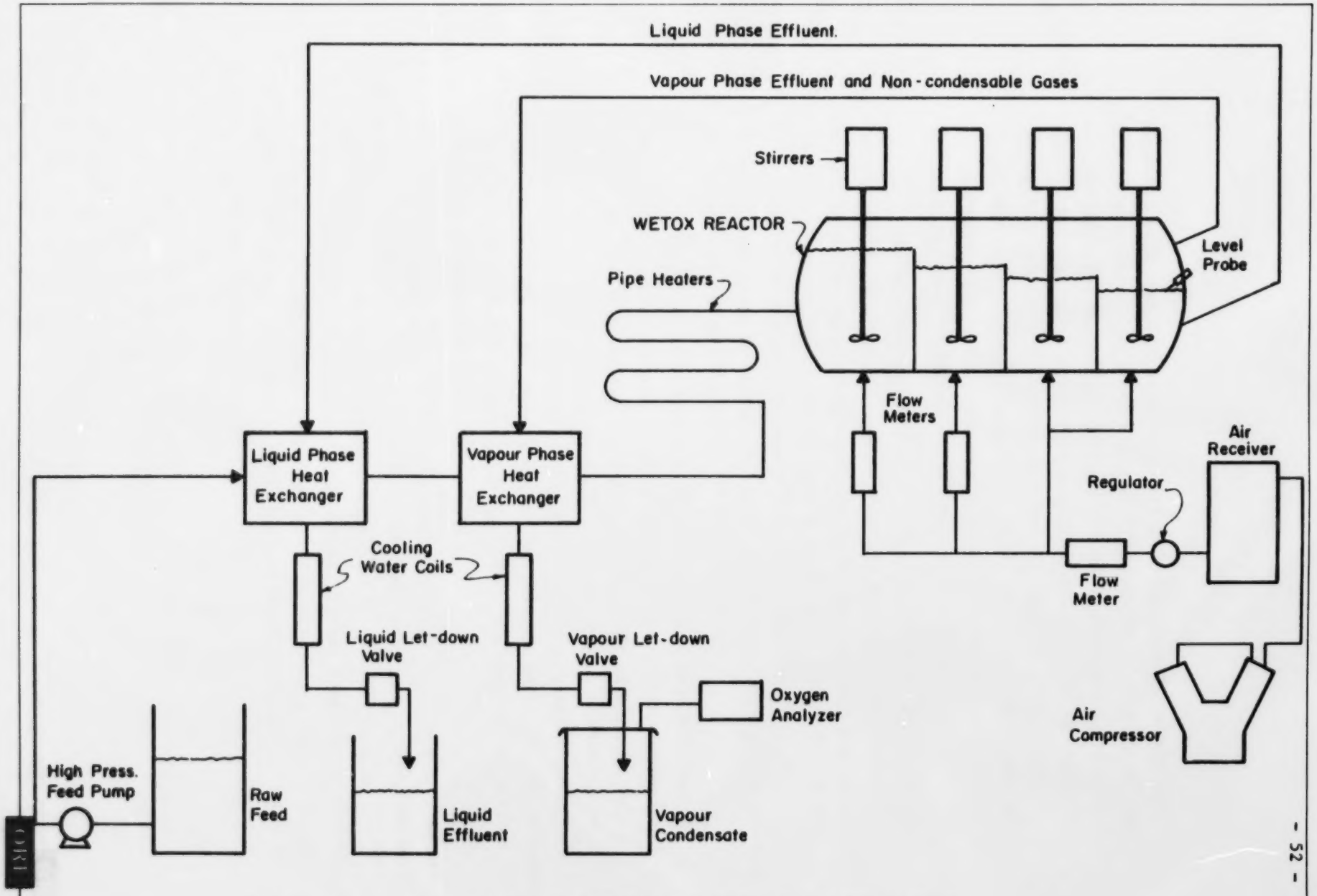

FIGURE 4.2 SCHEMATIC DIAGRAM OF WETOX PILOT PLANT

preheated such that following injection into the reactor, combustion will be initiated. This neces·itates bringing the pilot plant to the desired operating or reaction temperature prior to starting the feed of peat. The heat-up of the system is accomplished by pumping hot water through the system. The water is heated by external pipe heaters (9 kW) and electric immersion heaters inside the first compartment of the reactor (8 kW). Once the desired temperature in the reactor had been achieved, the feed of the macerated peat suspension was started.

The peat was pumped from a storage tank and metered into the pilot plant using a variable speed progressing-cavity pump (Moyno Model SSQ). The feed rate could be adjusted between about 600 mL/min and 1200 mL/min. The flow rate is monitored using a Fairbanks H-4100 load cell and an Action Instruments VIP 5524W weight monitor which converts the change in weight per unit time to a flow rate. The pressure in the reactor was maintained at 4.5 MPa (650 psig).

Referring to Figure 4.2, the raw peat was initially pumped through two heat exchangers in which the two hot effluent streams, liquid and vapour preheated the feed to about 188°C (370°F), or 44°C (80°F) below the reaction temperature. If additional preheating was required, external pipe heaters were used. The raw peat was then injected into the first compartment of the reactor, where, in the presence of oxygen and water, the peat ignited, thereby maintaining the desired reaction temperature.

Compressed air was added continuously to the reactor. The air was supplied from a Bauer K-15-10, 15 HP compressor at 6.9 MPa (1000 psig), regulated to reactor pressure and controlled to each of the four compartments with individual needle valves. Three flow meters were used to measure the air flow. Separate meters were used for the air to the first and second comparments, while a third meter measured the total air flow to the reactor.

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The four compartments in the reactor are each mixed mechanically with impellers rotating at 900 RPM. The compartments are separated by partitions, the liquid overflowing from one compartment to the next. The reactor is essentially four completely mixed reactors in series. The volume of the first compartment is 12 litres, while the remaining three are 8 litres each. Samples can be obtained from individual compartments, while the reactor is operating. This allows various residence times to be tested while maintaining the same feed rate.

There are two effluent streams from the reactor: a liquid phase and a mixture of vapour and non-condensable gases. The liquid effluent flow is controlled by a conductivity probe which automatically opens and closes an air operated needle valve as the liquid level in the reactor rises and falls. The flow of liquid effluent is, therefore, intermittent. This would not be true on a larger scale, where flow rates would be sufficient to allow truly continuous operation. The vapour phase effluent and gases are exhausted continuously through a Masoneilan back pressure control valve, after which the vapours are condensed and collected. The gases are vented to atmosphere. There was no air pollution problem encountered with the wet oxidation of peat. Analyses indicated only trace amounts of hydrocarbons in the off-gases; the sulfur compounds remain in solution as sulfate ions.

As previously mentioned, both effluent streams are used for preheating the raw peat prior to oxidation. In a larger plant, only a portion of the heat of combustion is required for the preheating duty. Refer to Section 7.1, which describes the design of a full-scale plant and the associated energy balance.

A variety of measurements and samples are obtained during the course of a continuous wet oxidation test. Every half-hour, temperatures were recorded from a number of locations: peat after preheating, in each reactor compartment and from both the liquid effluent and vapour effluent streams. The air flow rates and the percent of oxygen in the off-gases, as measured by a Taylor type OA 272 oxygen analyzer, were also closely monitored. A continuous display of the feed rate of peat was provided

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by the Visipak weight monitor. Periodically, the flow of vapour phase condensate was measured with a 2-litre graduated cylinder to determine the flow distribution between the two effluent streams.

Unfortunately, the design of the pilot plant was not ideally suited to application to peat. As described fully in later sections, the largest COD reduction occurs very quickly, generally in less than five or six minutes. Therefore, residence times of less than ten minutes would be acceptable for minimum reactor size. The sizing of the pilot plant equipment precluded residence times less than ten minutes since the maximum pumping rate was 1200 mL/min. There was also a limitation on reaction temperature and COD concentration of the feed. Ideally, the higher the COD concentration, the greater the temperature rise in the reactor due to the increased rate of burning. This results in a small reactor and less heat required for preheating the feed. However, with high COD concentrations and short residence times, a large amount of oxygen is required to support the combustion. This means that, unless very high pressures can be employed, there is excessive heat loss from the reactor due to the copious production of steam.

The pilot plant is limited to a maximum operating pressure of about 4.8 MPa (650 psig). In order to operate at 232°C (450°F), only a limited amount of air could be added without lowering the reaction temperature. Therefore, full strength feed solutions and short residence times could not be tested while still ensuring an excess of oxygen and maintaining reaction temperatures above 227°C (440°F). These limitations, of course, would not exist in a plant specifically designed for the wet oxidation of peat.

4.3 Results

4.3.1 Batch Experiments

4.3.1.1 Reaction Kinetics

Initial experiments were carried out in the 2-litre batch autoclave. The purpose of the experiments was to obtain a model for the reaction kinetics, determine the rate and extent of the reaction at various temperatures and to observe the effects of various wet oxidation catalysts.

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The concentration of oxidizable material in the feed and processed samples is conveniently represented by the COD determined according to the rapid method of Knechtel (1978), using chromic acid and catalyst. Total organic carbon (TOC) measurements were found to be unreliable, because the peat particles caused poor repeatability during the injection of samples into the TOC analyzer.

The state of oxidation and, therefore, the fuel value of most organic compounds, are reflected in their COD per unit weight. Zimmermann (1958) has shown that the COD of carbonaceous materials averages 13.9 MJ/kg COD. We found that the heating value of our peat samples ranged from 13.7 to 15.5 MJ/kg COD.

Figure 4.3 illustrates the typical course of a batch wet combustion reaction of a peat sample at 232°C. Complete wet combustion of peat slurries follows the usual course of wet oxidation reactions, observed in the treatment of sludges and mixed organic wastes: there is an initial rapid reaction, in the course of which 50-70% of the COD is oxidized within 5-12 minutes. The reaction that follows is much slower, and an additional 5-10% of the initially charged COD is oxidized during a total reaction time of 60 minutes. This second reaction is 10-20 times slower than the first one. There is usually a well-defined inflection point in the reaction curve, marking the completion of the initial reaction.

Such a configuration of data points, observed in most experiments (Appendix A) permits the simplifying assumption of considering plots of ln (COD) vs time as the sum of two lines, as shown in Figure 4.4. It is not intended to imply that the reaction is the sum of the two simple first-order reactions, but rather that this assumption is useful in characterizing the process and eases the task of organizing the experimental data.

To test this assumption, even if over a limited range only, experiments were carried out varying the initial concentration of the feed and the oxygen supply. Table 4.2 shows that the assumption of first order is reasonable for the initial reaction at least, provided that at least a stoichiometric equivalent of oxygen is supplied.

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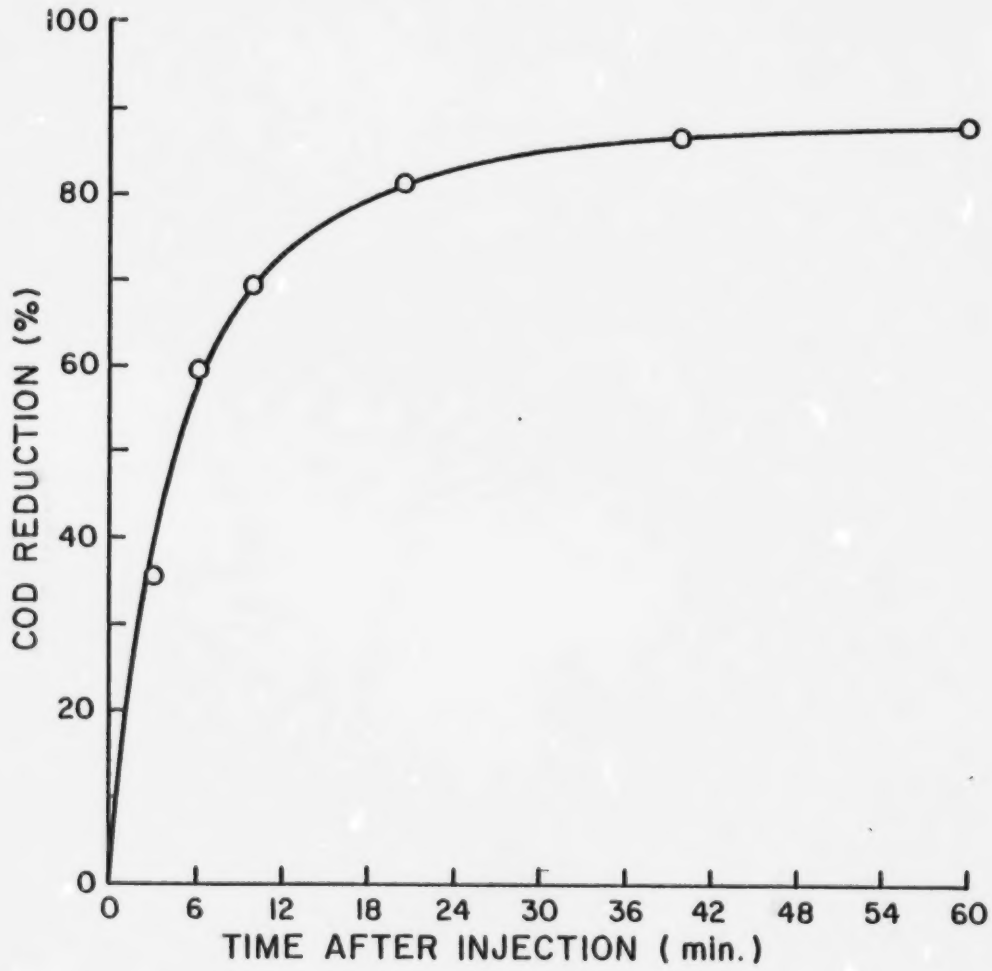

FIGURE 4.3 - Oxidation of Peat in a Batch Autoclave at 232°C, 4.48 MPa

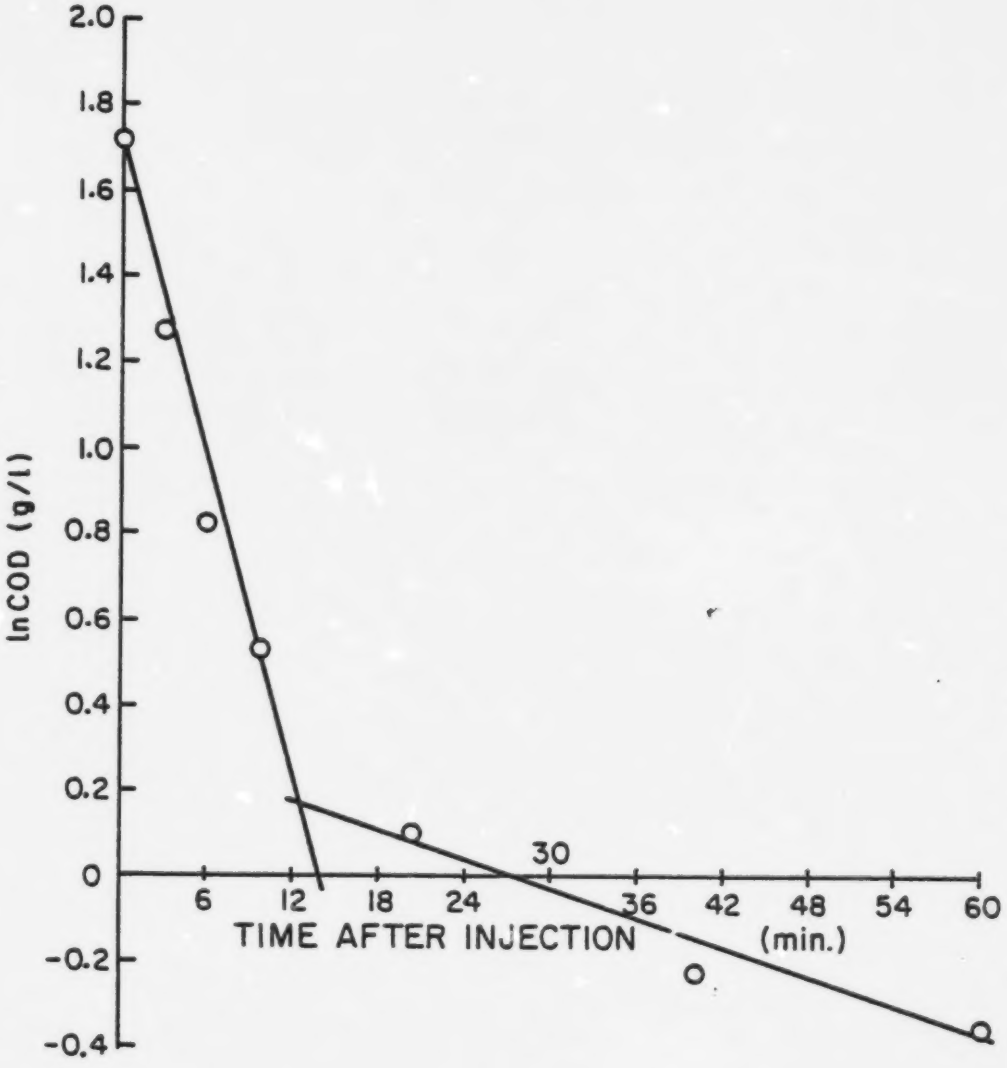

FIGURE 4.4 PLOT OF lnCOD vs TIME TO APPROXIMATE TWO Ist. ORDER KINETIC CONSTANTS. RATE CHANGE IS AT ABOUT 13 MIN. N. ONTARIO PEAT, 232°C, 4·48 MPa.

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TABLE 4.2 - Wet Oxidation of Manitoba Peat
Variation of Feed and Oxygen Concentration
Duplicate Samples

Temperature °C	Feed Concentration % COD	O_2/COD by wt.	K_1 min^{-1}	K_2 min^{-1}
260	2.64	3.34	0.260	0.0063
260	0.87	3.34	0.273	0.0023
260	0.87	1.1	0.258	0.0108

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If two first order reactions are assumed, then the oxidation of the peat may be modelled by these equations:

$$\frac{d(COD)}{dt} = -K_1(COD) \qquad \text{to the inflection point,}$$

and thereafter $$\frac{d(COD)}{dt} = -K_2(COD)$$

There are two first order kinetic constants, K_1 and K_2, for the fast and slow reaction regimes respectively. These constants were determined by plotting ln(COD) versus time and obtaining the slopes of the two intersecting straight lines. Figure 4.4 illustrates a typical graph. The intersection of the two straight lines indicates the time of the rate change from the fast to the slow regimes. The lines were fitted by the least squares method, and a minimum criterion of acceptability ($r = 0.95$) was observed to decide where to draw the lines.

The oxidation kinetics of three different peat samples were determined in batch experiments. The samples have been described in Section 4.2.1. The results of the experiments are summarized in Tables 4.3 to 4.5 for Northern Ontario, Manitoba and Newfoundland peats, respectively. The raw experimental data are given in Appendix A. The effects of differences in the peat samples are discussed in Section 4.4.1.2.

The temperature dependence of the first reaction constant, K_1, was modelled according to the Arrhenius relation -

$$K = Ae^{-E/RT}$$

where
- K = reaction rate constant, $minute^{-1}$
- A = frequency factor, $minute^{-1}$
- E = activation energy, calories/mole
- R = gas constant, calories/°K-mole
- T = temperature, °K

All three peat samples' initial reaction constant showed a good correlation by this method. The Arrhenius plots are shown on Figure 4.5 and the calculated activation energies, frequency factors and correlation coefficients are given in Table 4.6.

TABLE 4.3 - Total Oxidation Kinetics: Northern Ontario Peat

Temperature °C	η	K_1 min-1	K_2 min-1	Rate Change min	COD Reduction			
					Experimental		Calculated	
					@ 10 min	@ 20 min	@ 10 min	@ 20 min
121	1	---------- NO REACTION ----------						
149	1	---------- NO REACTION ----------						
177	2	0.039	0.014	16.2	35.5	43.6	32.3	49.6
204	2	0.059	0.017	8.6	40.0	52.0	41.0	50.6
232	8	0.130 σ = 0.039	0.0131 σ = 0.047	8.0	65.2 σ = 11.0	73.0 σ = 10.6	65.6	69.8
246	6	0.191 σ = 0.027	0.0135 σ = 0.065	5.8	67.8 σ = 7.5	73.4 σ = 7.9	68.7	72.7
260	8	0.217 σ = 0.048	0.0069 σ = 0.002	5.4	69.7 σ = 6.9	74.3 σ = 7.2	69.9	72.0
271	5	0.250 σ = 0.036	0.0141 σ = 0.006	4.7	70.9 σ = 8.9	77.5 σ = 5.3	71.3	75.1

NOTES: η = number of data points
σ = standard deviation

TABLE 4.4 - Total Oxidation Kinetics: Manitoba Peat

Temperature °C	η	K_1 min^{-1}	K_2 min^{-1}	Rate Change min	COD Reduction			
					Experimental		Calculated	
					@ 10 min	@ 20 min	@ 10 min	@ 20 min
232	2	0.136	0.0093	10.4	74.2	77.3	74.3	77.8
246	2	0.185	0.0082	8.0	77.9	81.5	77.6	79.3
260	2	0.260	0.0063	5.5	77.5	81.4	76.7	78.1
271	2	0.323	0.0053	5.5	83.3	86.3	83.5	84.4

NOTE: η = number of data points

TABLE 4.5 - Total Oxidation Kinetics: Newfoundland Peat

Temperature °C	η	K_1 min^{-1}	K_2 min^{-1}	Rate Change min	COD Reduction			
					Experimental		Calculated	
					@ 10 min	@ 20 min	@ 10 min	@ 20 min
221	3	0.179	0.0096	3.9	54.4	58.5	53.5	57.7
232	3	0.229	0.0092	3.5	57.9	61.5	58.6	61.8
246	3	0.236	0.0105	3.6	60.5	65.0	60.9	64.3
252	3	0.260	0.0095	3.8	60.0	65.8	61.7	64.7
260	3	0.275	0.0084	3.7	63.9	68.0	64.8	67.5
271	3			3.6	67.1	69.7	65.3	68.3

NOTE: η = number of data points

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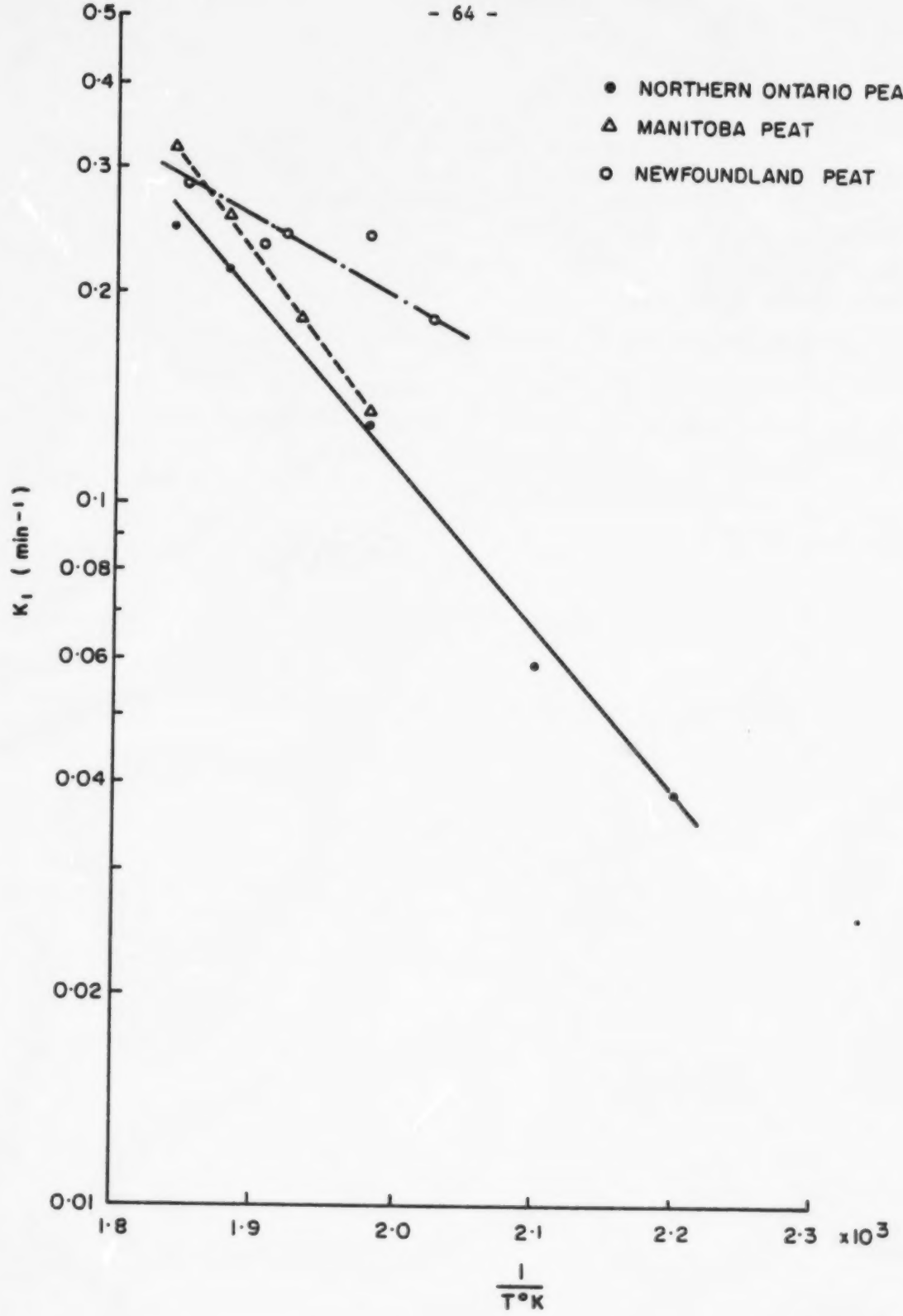

FIGURE 4·5 ARRHENIUS PLOT OF K_1 VALUES

TABLE 4.6 - Total Oxidation of Peat Activation Energies According to Arrhenius' Model

Source of Sample	E cal/mole	A min^{-1}	r
Northern Ontario	- 10401	4111	- 0.991
Newfoundland	- 3106	4.8	- 0.974
Manitoba	- 12418	32700	- 0.999

NOTES: E = activation energy
A = frequency factor
r = linear regression correlation coefficient

The second reaction constants, K_2, showed no such correlation with temperature. In the case of Northern Ontario peat, no clear trend of temperature was evident, Newfoundland peat showed no temperature dependence in K_2, and the K_2 values of Manitoba peat appeared to decline with increasing temperature. Simple organic acids are produced after the initial fast reaction. These acids (mainly acetic) are refractory to wet oxidation at the temperatures employed in these experiments and the COD test is insufficiently accurate to clearly show the expected increasing trend in K_2 with rising temperature.

4.3.1.2 Catalytic Effects

It is known from our previous experience with wet oxidation that acidic conditions (< pH 4) and/or certain metal catalysts increase the rate of the initial reaction. Since all the peat samples were initially quite acidic (∿ pH 4) and the pH further declined in the course of the reaction (Table 4.12), no experiments were necessary to examine separately the effect of acid addition.

Copper, cobalt and nickel ions were tested for their catalytic effect at 400 mg/L at 232 and 271°C. Nickel and cobalt showed no catalytic effect at 232°C; nickel showed an accelerated initial reaction at 271°C. Copper, on the other hand, showed a clear positive catalytic effect at both temperatures. Copper catalyst was examined more closely in the case of both Ontario and Manitoba peats. The results are shown in Tables 4.7 and 4.8. The effect of copper catalysts will be examined in continuous flow experiments in Section 4.3.2 and 4.4.2.

Peat deposits are known to adsorb dissolved metal ions from the bog-water. In order to look for the presence of catalytic amounts of metals in the peats as well as serendipitous enrichment of valuable metals, the three peat samples were subjected to a multi-element analytical scan (Tables 4.9, 4.10). The majority of the elements were analyzed by DC plasma emission spectrometry on an aqua regia leach of the ashed material. The results reported represent the aqua regia leachable material.

Although the concentrations of some elements show wide variation among the peat samples, none of the metals are present in commercially

TABLE 4.7 - Catalyzed Wet Oxidation Kinetics: Manitoba Peat

Catalyst mg/L	Temperature °C	K_1 min^{-1}	K_2 min^{-1}	% COD Reduction		Rate Change min	Feed Concentration % COD	O_2/COD by Weight
				@ 10 min	@ 20 min			
Ø	232	0.136	0.0093	74.2	77.3	10.4	2.48	3.34
50 mg/L Cu++	232	0.186	0.0046	77.4	84.5	10.4	2.6	3.34
200 mg/L Cu++	232	0.209	0.0068	88.3	91.2	10.4	2.97	3.30
300 mg/L Cu++	232	0.222	0.014	89.1	91.7	10.0	2.97	3.30
400 mg/L Cu++	232	0.231	0.0068	90.1	91.7	10.0	2.60	3.34
600 mg/L Cu++	232	0.236	0.019	90.6	92.8			
400 mg/L Ni++	232	0.148	0.0051	77.3	83.5	10.8	2.6	3.34
400 mg/L Co++	232	0.146	0.0101	76.7	81.4	8.0	2.6	3.34
Ø	271	0.323	0.0053	83.3	86.3	5.5	2.64	3.34
400 mg/L Cu++	271	0.558	0.014	95.4	96.2	5.6	2.6	3.30
400 mg/L Ni++	271	0.430	0.011	90.9	92.7	5.6	2.6	3.34
400 mg/L Co++	271	0.200	0.0051	86.5	89.1	10.0	2.6	3.34

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TABLE 4.8 - Copper Catalyzed Wet Oxidation Kinetics:
Northern Ontario Peat - 232°C

Catalyst mg/L Cu++	K_{1-1} min	K_{2-1} min	% COD Reduction		Rate Change min	Feed Concentration % COD	O_2/COD by weight
			@ 10 min	@ 20 min			
0	0.130	0.0131	65.2	73.0	9.6	0.496 - 0.635	19.9 - 25.5
100	0.177	0.0148	74.0	79.8	7.8	0.520	24.3
200	0.207	0.0101	80.8	85.6	8.7	0.520	24.3
300	0.255	0.015	83.8	87.4	6.6	0.555	22.7
400	0.286	0.022	83.8	89.2	6.0	0.555	22.7
600	0.267	0.0101	84.9	89.5	7.5	0.496	25.8

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TABLE 4.9 - Leachable Trace Elements in Peat Samples

Element	Concentration Expressed as a % of the Ash		
	Western Peat	Northern Peat	Newfoundland Peat
Co	0.011	0.001	0.0019
Zn	0.026	0.015	0.00503
Cd	0.003	0.001	0.000317
B	0.003	0.001	0.00336
Bi	0.001	0.001	0.00155
P	0.339	0.341	0.7816
Be	0.001	<0.001	<0.001
Fe	10.6	1.33	1.5531
Mn	0.034	0.007	0.5997
Ca	2.67	1.24	5.2293
Mg	1.22	0.236	0.4014
Cu	0.018	0.014	0.00809
Al	6.90	3.64	0.2491
V	0.020	0.011	0.00307
Mo	0.006	0.001	0.00225
Pb	0.007	0.010	0.00173
Ni	0.027	0.036	0.00322
Cr	0.010	0.008	0.00104
Na	0.395	0.244	0.0965
Ash - % of dry solids	13.6	12.6	10.1

TABLE 4.10 - Leachable Noble Metals in Ash

Element	Concentration, % by weight of Ash		
	Newfoundland Peat	Western Peat	Ontario Peat
Au	0.000185	0.000122	0.000119
Ir	0.000973	0.000565	0.000445
Pt	0.000439	0.000188	0.000109
Pd	0.00037	0.000199	0.000168
Os	ND	ND	ND
Ru	0.00149	0.000356	0.000282
Re	0.00187	0.000265	0.000005
Rb	0.000249	0.000127	0.00006
Ag*	<0.00005	<0.00005	<0.00005

*Flame atomic absorption spectrophotometry

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significant quantities. The metals thought to have catalytic effects on wet oxidation (Cu, Ni, CO, Cr, Pt group) are not present in sufficient amounts to account for the variation in the oxidation kinetics.

4.3.1.3 Effects of Sample Preparation

The peat samples were homogenized in a Waring blender or in a macerating pump prior to injection into the batch autoclave or the pilot plant reactor. As mentioned in Section 4.2.2, microscopic particle size analysis could not be carried out on these samples. The purpose of this set of batch experiments was to examine the effects of sample preparation on the kinetics of oxidation, and to confirm the fact that there was no significant variation in the batch and continuous kinetics which could be ascribed to sample pretreatment.

Three samples were taken of the Northern Ontario peat: "raw", from which hard woody pieces were picked by hand; "macerated" which was a sample of pilot reactor feed recirculated with the macerating pump and "blended" which was processed in the Waring blender as usual. Similar concentrations of each material were placed into the 2-litre batch reactor ($\sim$ 6 g/L CCD) and heated to 232°C. As the reactor reached operating temperature, oxygen was injected. Samples were withdrawn at various times and analyzed for total and soluble COD. Reaction kinetics were calculated in the customary manner, taking the time the reactor reached operating temperature as the starting point.

The results in Table 4.11 show that raw peat reacts slower than the two comminuted samples. The latter show no significant difference in reactivity between themselves. Considerable solubilization and some reduction in TCOD takes place during heat-up, which takes about 40 minutes.

Comparison of the K_1 with customarily injected (no heat-up) samples show that other transformations also take place during the long heat-up time which slow down the rate of oxidation subsequently. The residence time in the preheat section of the pilot plant reactor is less than two minutes. Therefore, the experimental technique of injecting homogenized peat samples into the batch reactor is thought to be valid.

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TABLE 4.11 - Effect of Sample Preparation Method on Reaction Kinetics
Northern Ontario Peat - 232°C

Sample	K_1 min^{-1}	K_2 min^{-1}	Rate Change min	Initial		At Time 0	
				TCOD mg/L	SCOD mg/L	TCOD mg/L	SCOD mg/L
Raw*	0.043	0.0079	14.6	5540	74	5190	2200
Macerated*	0.089	0.011	6.3	5000	106	3940	1170
Blended*	0.071	0.0095	10.4	6350	215	5310	1730
Injected**	0.130	0.0131	8.0	-	-	-	-

*Sample heated up in reactor over 40 minutes in the absence of oxygen
**Customary method of sample injection, shown for comparison

The slight reduction in TCOD in the absence of oxygen during heat-up is attributed partially to the formation of products which are refractory to the COD test, partially to the vapourization of incompletely oxidized molecular fragments.

4.3.1.4 Intermediate Products of Oxidation

The wet oxidation process is thought to proceed in two consecutive steps: initial rapid oxidation of carbonaceous materials to CO_2, water and intermediates. These intermediates, which are thought to be simple organic acids, then oxidize slowly in the second stage of the reaction.

In order to shed some light upon the nature of the reactions, we followed the concentrations of total and soluble COD in the course of a batch reaction. Further, we tested the assumption that the soluble refractory materials are primarily simple organic acids.

The reaction was performed as in 4.2.1.3 on Northern Ontario raw, macerated and blended peats. The three curves were very similar. Therefore, only one is reproduced in Figure 4.6.

The treated samples were analyzed by high pressure liquid chromatography for the identification and quantitation of organic acids in the soluble portion. The experimental method and detailed findings are reproduced in Appendix B. Formic and acetic acids were indeed the most abundant ones present. However, when the COD equivalent of all the acids identified was calculated, only about one third of the residual SCOD could be accounted for by them. Therefore, there must be other materials present which exert COD but which are caught in the pretreatment column of the instrument, or which are removed in the different methods of sample preparation.

It is clear from Figure 4.6 that the acids are resistant to oxidation under the conditions of the experiment and that their concentration peaks at the time of rate change.

A typical set of results obtained in the total oxidation of Newfoundland peat is shown in Table 4.12. The rapid generation and slow oxidation of acids may be seen from the change of pH in the course of the reaction.

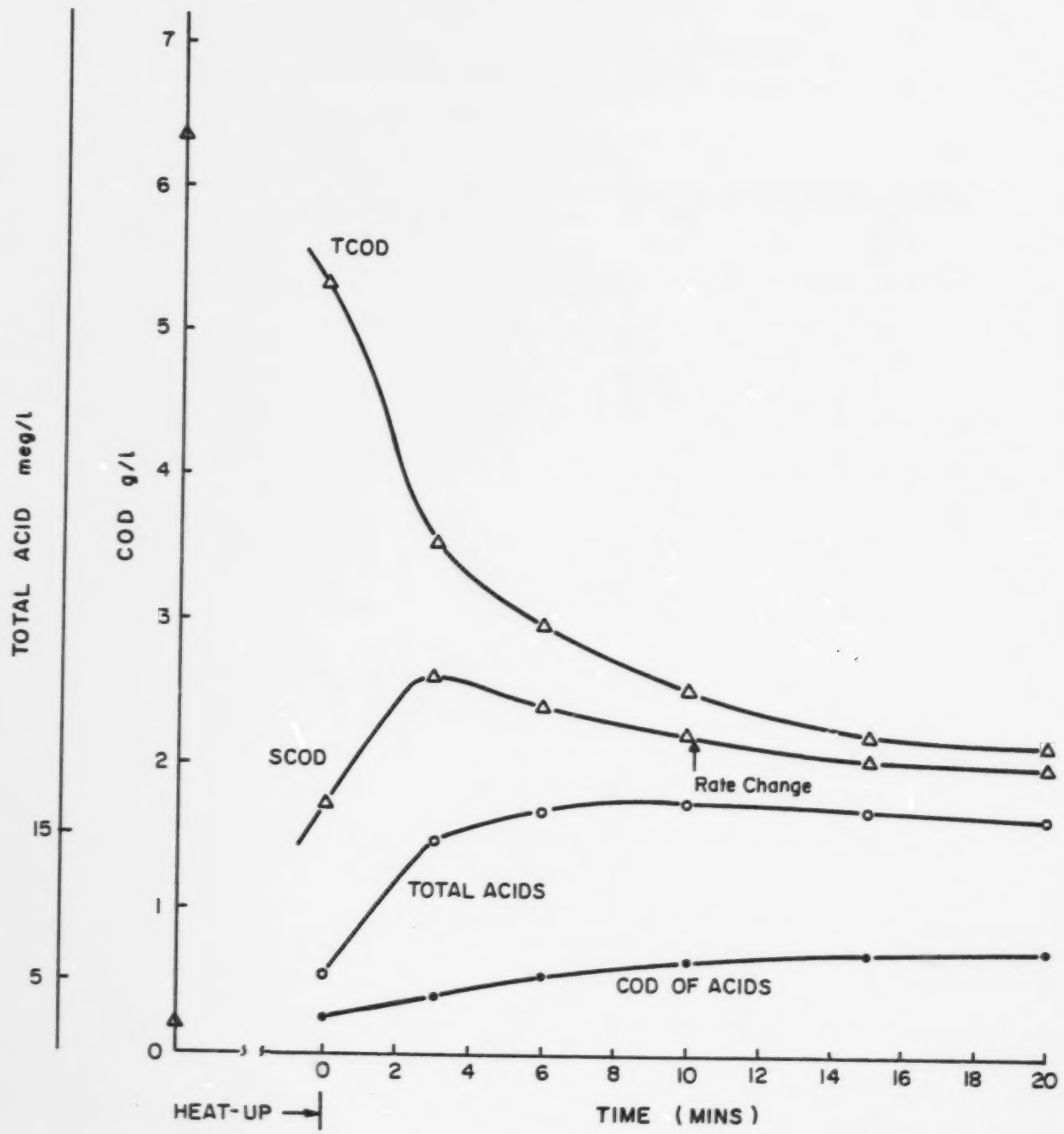

FIGURE 4·6 NORTHERN ONTARIO BLENDED PEAT BATCH OXIDATION AT 232°C.

TABLE 4.12 - Typical Course of Total Oxidation: Newfoundland Peat, 232°C, 4.58 MPa

Time min	pH	COD mg/L	COD Reduction %	SS mg/L	TS mg/L	Ash % TS
0	4.1	6233	0	NA	4908	11.2
3	2.9	3030	51.4	740	1940	26.2
6	2.95	2910	53.3	610	1690	29.6
10	3.05	2610	58.1	510	1490	33.6
15	3.15	2500	59.9	480	1360	36.7
20	3.4	2400	61.5	450	1300	37.5
40	4.0	2050	67.1	320	1090	43.5

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4.3.2 Continuous Flow Pilot Plant Experiments

The continuous wet oxidation of peat was investigated using the 36-litre pilot plant. A number of key process variables were tested:

(i) Hydraulic Residence Time
(ii) Oxygen Supply
(iii) Copper Catalyst Concentration
(iv) Initial COD Concentration

These tests were also used to verify the validity of the batch kinetic analysis at 232°C. Because of certain mechanical limitations of the pilot plant, large variations in the reaction temperature were not possible. Therefore, the key process variables were tested at a single temperature and pressure, 232°C and 4.48 MPa (450°F and 650 psig). A general summary of the continuous flow experiments is presented in Table 4.13, the results arranged in chronological order.

The specific effects of each of the key variables were investigated by selecting a series of experiments in which the reaction conditions differed in only one of the variables. Because of the large number of possible combinations, it was beyond the scope of this project to study in detail the interrelationships between all four parameters.

The criterion used to evaluate the effects of process changes was the extent of COD reduction expressed as a percentage of the starting COD concentration. It is believed that this is the most important factor for recovering energy from peat through wet oxidation. In the presence of oxygen, COD reduction is directly related to heat production, releasing 13.9 MJ/kg COD of heat per pound of COD removed (6000 Btu/lb COD).

4.3.2.1 Hydraulic Residence Time

The effect of residence time was investigated with experiments designated G1, G2 and G3. The initial concentration of COD was 86 g/L. The feed rate was maintained at 0.98 L/min corresponding to total residence times of 12, 20 and 29 minutes in the first, second and third compartments respectively. The rate of COD

TABLE 4.13 - Summary of Continuous Wet Oxidation Pilot Plant Results

No.	Feed Rate (L/min)	TCOD Conc. (g/L)	Catalyst Conc. (mg/L)	Residence Time (min)	Reaction Temp. (°C)	COD Red. (% of Feed)	Gas Supply (L/sec)	COD/O_2 (g/g)	Notes
A	1.20	75	0	17	224	52	3.30	1.11	1, 2
B	0.48	115	0	25	232	61	1.32	1.79	6
C	0.68	140	0	29	232	62	1.75	2.08	2, 6
D1	0.80	86	0	15	232	39	1.13	1.64	6
D2	0.60			20		47		1.47	6
E	0.60	130	0	20	243	63	0.57	1.43	3, 6
F	0.68	83	0	29	232	55	0.99	2.08	2, 6
G1	0.98	86	0	12	232	62	1.23	1.20	4, 6
G2				20		65	1.46	1.05	2,4,6
G3				29		70	1.56	1.06	4,5,6
H1	0.60	97	200	20	232	63	1.32	2.40	
H2				33		67	1.79	1.88	2, 6
H3		83	400	20		66	1.42	2.12	
H4				33		66	1.89	1.60	2, 6

1 - Western (Manitoba) peat used
2 - Two reactor compartments used
3 - Gas supply composed of pure oxygen
4 - Gas supply composed of 60% oxygen, 40% nitrogen
5 - Three reactor compartments used
6 - Northern Ontario peat used

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reduction corresponded closely to the rate of oxygen utilization, indicating sufficient oxygen was available for the reaction. This was accomplished by using a 60% oxygen, 40% nitrogen mixture as the gas supply.

The COD reduction, as a function of the residence time, is illustrated in Figure 4.7 as curve #1. It appears that, once the transition has occurred from the fast to the slow reaction regimes (refer to Section 4.3.1.1), there is little benefit to be gained from increased retention times. Increasing the overall residence time from 12 to 29 minutes resulted in increasing the COD reduction from 62% to 70%, an increase of only 13%. Residence times shorter than twelve minutes could not be tested due to limited pump capacity. These results conform closely to those predicted by the batch testing.

The effect of residence time is also seen in curve #2, Figure 4.7, obtained from the results of experiments D1, D2 and F. Compressed air was used as a source of oxygen. As a result, sufficient oxygen could not be transferred to the reaction mixture without excessive heat loss due to steam production. These effects are further discussed below.

4.3.2.2 Oxygen Supply

The overall effect of insufficient oxygen on wet oxidation is clearly evident from Table 4.13 and Figure 4.7. The percent reduction in COD as a function of residence time will be influenced by the availability of oxygen. With about equal starting COD concentrations, experiment G3 achieved 70% COD reduction in 29 minutes, compared to only 55% in the same time during experiment F. Compressed air was used as the oxygen supply in experiment F. At least half of the COD reduction was accomplished without using the externally supplied oxygen.

This oxygen starvation is evident from the ratio of COD reduction to the amount of oxygen consumed. This ratio varies between 1.0 for a uniform oxygen distribution throughout the reactor, achieved with pure

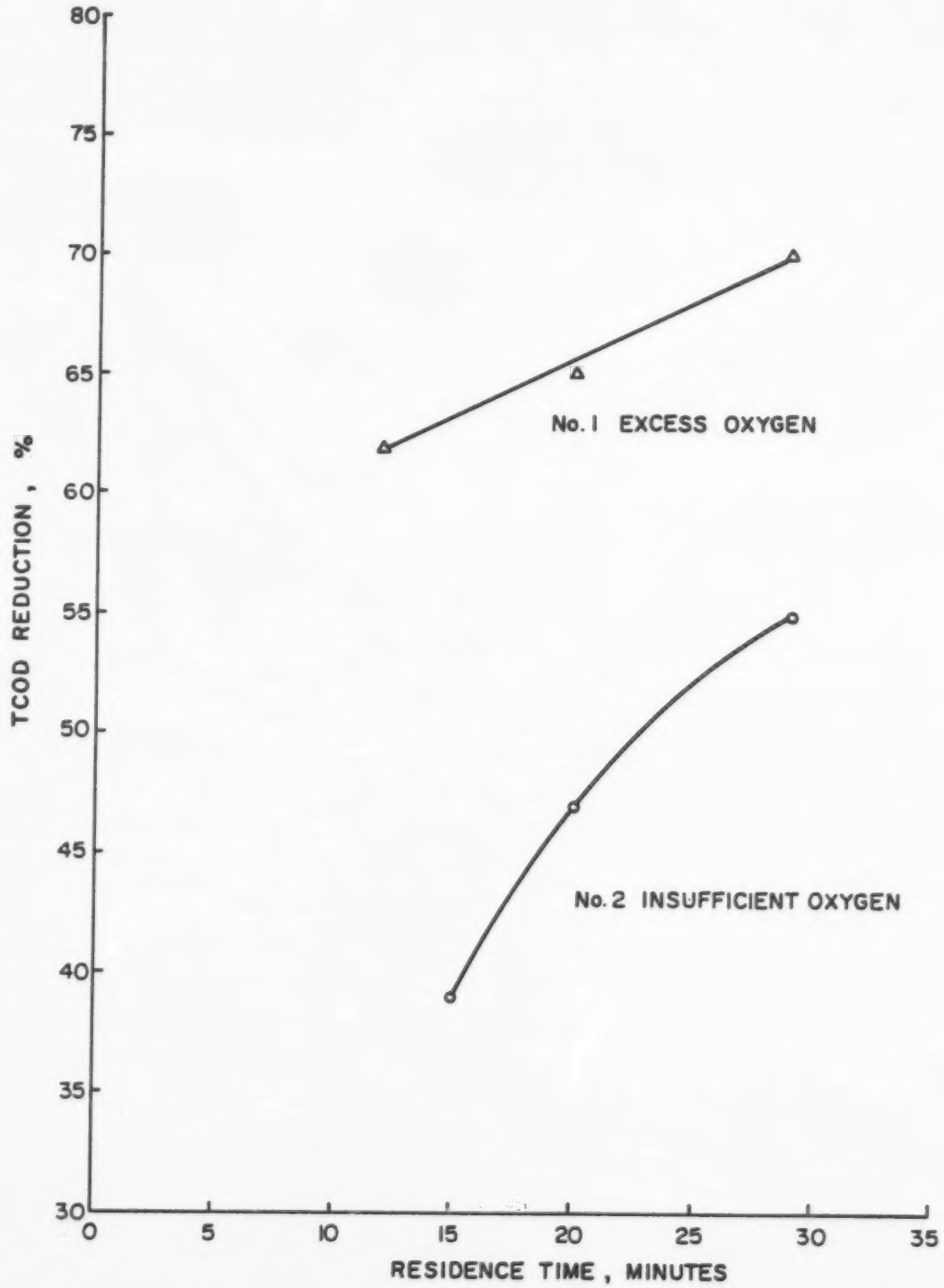

FIGURE 4.7 CONTINUOUS WET OXIDATION OF NORTHERN ONTARIO PEAT, EFFECT OF RESIDENCE TIME.

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oxygen, to about 2.0 in experiments C and F where compressed air was used. Under these O_2-starved conditions, COD reduction still occurs, albeit slower and not to as great an extent. Because this COD reduction cannot be considered as true wet combustion, there is not likely to be as much heat generation during the reaction. When previously observed during wet carbonization of peat, it was thought to be a result of decarboxylation. However, in this case, it is difficult to account for that magnitude of COD reduction by that mechanism alone.

In conclusion, adequate oxygen supply must be maintained. In order to avoid the use of oxygen enriched gas feed, the agitator design must be optimized in future designs to provide sufficient dissolved oxygen in the viscous peat slurry.

4.3.2.3 Copper Catalyst

Experiments H1 through H4 were conducted with two concentrations of copper catalyst, 200 and 400 ppm of Cu^{++}. It appears from Table 4.13 that there is some advantage in using copper to achieve greater COD reductions when residence times of 20 minutes or longer are used. Comparison with an experiment performed under similar conditions with no catalyst, D2, indicates that, with air as the oxygen source, 200 ppm of copper will increase the COD reduction from about 47% to 63% in 20 minutes. This reduction is essentially the same as was achieved with no catalyst and excess oxygen (G2). The pilot plant was not operated with both a catalyst and excess oxygen. However, results from the batch tests indicate further improvement may be possible. Refer to Section 4.3.1.2.

The effect of the catalyst was less pronounced with longer residence times, although significant improvement was still achieved, 67% COD reduction in experiment H2 after 33 minutes compared to 55% COD reduction after 29 minutes in experiment F. As indicated in experiments G1 to G3 with excess oxygen, COD reduction appears to plateau between 65% and 70%. It is, therefore, likely that use of a catalyst may decrease residence times. However, the ultimate COD reduction will not increase.

The catalyst concentration was increased to 400 mg/L for experiments H3 and H4. It is evident that the plateau was reached before 20 minutes and that no further COD reduction was achieved. Increasing the catalyst concentration may, therefore, result in a further decrease in the required residence time but, again, without achieving an overall increase in the extent of the reaction.

4.3.2.4 Initial COD Concentration

If the reaction behaves kinetically as first order with respect to COD concentration as demonstrated with the batch testing, then, after a given residence time, the COD reduction (expressed as percentage of the starting COD) will be independent of the starting COD concentration. However, the solids content of the raw peat slurry, hence COD concentration, will influence other process parameters.

There are both advantages and disadvantages to using concentrated feed slurries. A high solids slurry is difficult to pump, preheat and mix and could result in inefficient combustion. In addition, since COD reductions are always a percent of the starting concentration, the liquid effluent would have relatively high concentrations of refractory compounds that could cause problems for subsequent biological treatment. On the other hand, a concentrated feed reduces the size of the reactor and can result in greater energy recovery since less heat is required for preheating the incoming slurry.

The pilot plant was operated with three different starting COD concentrations with otherwise essentially identical conditions. The starting feed concentrations tested were: 83 g/L, 140 g/L and 180 g/L of COD, prepared from macerated Northern Ontario peat. Results from the first two experiments are presented in Table 4.13, numbers F and C respectively. Conditions were 232°C with a hydraulic residence time of 29 minutes in two reactor compartments. Air was used as an oxygen source. Unfortunately, mixing and oxygen transfer limitations in the pilot plant

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apparently prevented combustion from initiating in the most concentrated slurry. Therefore, these results have not been included in the Table. Because of various physical constraints, such as pumpability and oxygen transfer, it is not likely that a raw peat of 180 g/L of COD or 13% solids could be processed. The COD/O_2 ratio shows that both experiments F and C were proceeding under oxygen limited conditions. In such cases, the first order assumption may not be valid.

4.4 Discussion

4.4.1 Batch Experiments

4.4.1.1 Reaction Kinetics

The reactions occurring in the course of wet oxidation are complex and not well understood. However, from the work of other authors (Chowdhury, 1974; van Amstel, 1973) and our own observations of the wet oxidation of a variety of materials, it is postulated that the following generalized reaction scheme may be occurring:

$$\text{Carbonaceous material} + \text{Oxygen} \xrightarrow{K_a} CO_2 + H_2O + \text{Heat} \qquad \text{R1}$$

$$\text{Carbonaceous material} + \text{Oxygen} \xrightarrow{K_b} \text{Organic Acids} + \text{Heat} \qquad \text{R2}$$

$$\text{Organic Acids} + \text{Oxygen} \xrightarrow{K_2} CO_2 + H_2O + \text{Heat} \qquad \text{R3}$$

The parallel reactions 1 and 2 result in the initial rapid oxidation of peat and their combined rate gives rise to K_1. The organic acids formed by reaction 2 are refractory to wet oxidation, and their oxidation is observed in the second, slow stage of the wet combustion process, with the reaction rate expressed by K_2.

In Figure 4.6, it is shown how the organic acids are generated early in the course of the reaction and that they diminish only slowly with time. However, it is also evident from Figure 4.6 that there are additional, perhaps colloidal, materials present in the soluble fraction

which are resistant to oxidation. These observations contradict those of van Amstel (1971), who has found that the oxidation kinetics of fresh and thermally hydrolyzed sewage sludge were very similar.

In a well stirred system, where the oxygen supply has been maintained in excess of stoichiometric requirement, the kinetics of wet oxidation can be adequately represented (for the sake of simplicity) by first order kinetics according to the following equation:

$$\frac{dc}{dt} = - KC$$

where C = concentration of fuel expressed as the chemical oxygen demand, mg/L; t = reaction time, minutes; K = specific reaction rate constant, minutes^{-1}. The above equation, upon integration, yields

$$\ln \frac{C}{C_o} = Kt$$

where C_o = initial concentration of fuel (initial COD), mg/L. The specific reaction rate constants for each experiment have been calculated by plotting the logarithm of the ratio C/C_o against t and correlating the data points by the least squares method. A typical plot is shown in Figure 4.4. The data points plotted rather well into two straight lines (minimum correlation coefficient, r = 0.95). Although it would not be correct to imply that the mechanism is the sum of two simple first order reactions, assuming such a simplified model does correlate the data reasonably well and eases the task of calculating the temperature dependence of the reactions.

The observed average values of the specific rate constants for both the fast and slow reactions, represented by K_1 and K_2 respectively, are presented in Tables 4.3 through 4.5. The observed time where the fast reaction has run its course and the fast rate changes into the slow reaction rate is an important parameter used for the prediction of the extent of reaction. The fast reaction rate constant, K_1, is used up to the time of the rate change; thereafter the rate constant K_2 is applied. Using this model, the experimentally observed and calculated COD reductions agree rather closely for the batch reactions (Tables 4.3 through 4.5). The time of rate change is also used in the attempt to

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transfer batch data to predict the extent of reaction in the continuous flow reactor. It gives a quantitative indication of the easily combustible portion of the peat.

The temperature dependence of K_1 is well correlated using the Arrhenius equation:

$$K = A\, e^{\frac{-E}{RT}}$$

where K = rate constant, $minute^{-1}$; A = frequency factor, $minute^{-1}$; E = activation energy, calories/mole; R = gas constant, calories/°K-mole and T = temperature, °K. The Arrhenius plots are shown in Figure 4.5; the calculated activation energies and frequency factors are given in Table 4.6.

The temperature dependence of the rate of the slow reaction could not be correlated with the Arrhenius law, since the trends with temperature were paradoxical, as described in Section 4.3.1.1.

The activation energies obtained for the highly decomposed Manitoba and Ontario peats indicate that mass transfer processes are limiting factors in the reaction. The activation energy of Newfoundland peat showed an even lower value, probably indicating that the reaction took place at the surface of solid particles rather than colloidally dispersed ones as may be the case with the highly decomposed Ontario and Manitoba peats. For sewage sludge and sewage, van Amstel (1973) and Chowdhury (1974) obtained activation energies in the order of 23000 cal/mole.

Positive catalytic effects were demonstrated with the use of up to 400 mg/L copper ion at 232°C. Cobalt and nickel showed no catalytic activity at this temperature. However, at 272°C, nickel at 400 mg/L ionic concentration doubled the uncatalyzed reaction rate. There was a beneficial effect not only on the rate of catalyzed reactions, but also on the extent to which the reaction would proceed in a given time period. Both Ontario and Manitoba peats would reach over 90% COD combustion in the presence of 400 mg/L copper ion, contrasting with 65.2

and 74.2% respectively without catalyst. Nevertheless, the use of catalysts in these concentrations is not practical, on account of the cost of application and the need for removal prior to further processing of the peat slurries.

4.4.1.2 Effects of Peat Characteristics

The composition of peat varies with location and depth even within a given peat bog. Variations from one peat deposit to another are likely to be much greater. To minimize variability of experimental results, the peat samples (about one tonne of each) were dug from a small area, making sure that they were homogenous as far as possible with regard to humification grade and botanical make-up.

Peat contains an enormously complex mixture of organic materials, in which the chemically more stable residues of plant tissues are prominent. These substances may be classified by suitable analytical techniques into bitumens, humic acids, carbohydrates, proteinlike substances and lignins (Fuchsman, 1980). It is possible that the reactivities of these classes of compounds are different in wet oxidation; however, it was not possible, nor was it deemed necessary at the outset of the programme to correlate the reaction kinetics with this much compositional detail. Instead, the gross characteristics of degree of decomposition and botanical origin were used to describe the three peat samples in Section 4.2.1. In addition to these, the peat ash was analyzed for a large number of trace elements to determine if any are present in significant amounts, possibly accounting for catalytic effects (Section 4.3.1.2).

The criteria which can be compared among different peat samples are the reproducibility of experimental findings, kinetic constants, the extent of reaction after a certain time, the time of rate change and the effects of catalysts.

Ontario peat gave somewhat scattered results in the kinetic studies. Therefore, a considerable number of replicate experiments were done and the results were averaged (Table 4.3). These then gave good agreement between the average experimental and predicted values for the extent of reaction. The Newfoundland and Manitoba peats gave more consistent results.

The first kinetic constants of Ontario and Manitoba peat were similar over most of the temperature range examined, as were the times of rate change. Manitoba peat appeared to contain a larger amount of rapidly combustible material, judging from the extent of reaction after 10 minutes, which reached 83.3% in the case of Manitoba peat, compared with only 70.9% in the case of Ontario peat at 271°C. The temperature sensitivity of the reaction rates (K_1) were also similar, judging from the Arrhenius plots (Figure 4.5). The rate change times shortened as the temperature (and K_1) increased, with only a moderate increase in the extent of reaction, showing that probably the same combustion reactions were proceeding faster rather than additional components becoming available for reaction at higher temperatures. Little useful information could be extracted from the values of the second kinetic constants, which did not show regular trends with changes in temperature.

Newfoundland peat was not only rather different in botanical origin from the other two samples, but it was only of medium degree of humification (H5-6). There appeared to be less wet-oxidizable material present, judging from the extent of reaction which was less at corresponding temperatures than in the case of the highly humified samples (Table 4.5). Whatever combustible material was there, burned faster than in the case of the other two samples: the first kinetic constants were generally higher than the others at corresponding temperatures. The temperature dependence of K_1 was less, however, suggesting the effect of oxygen mass transfer limitation. Since both stirring rate and oxygen supply was similar for all samples, we can

conjecture that the less humified peat consists of more of solid rather than colloidal particles, and the reaction occurs at the interface of solid and liquid, giving rise to less temperature sensitivity for the overall process.

Summarizing the above findings, peats of similar degree of humification and botanical origin tend to behave similarly in their reaction kinetics. Whether the different behaviour of the Newfoundland peat is due to its different botanical make-up or its lesser degree of decomposition, cannot be decided on the basis of available data.

4.4.2 Continuous Flow Experiments

Since batch testing is much more readily performed than complex continuous-flow experiments, there is a great advantage if a consistent relationship can be demonstrated between batch and continuous kinetics. The batch system would be readily employed to test a wide variety of process conditions and these results would be mathematically transformed for process evaluation in a continuous flow system.

The method used in this transformation is that described by Jones (1951). It is a graphical method that determines the extent of reaction occurring in each of a series of continuously fed agitated vessels given the reaction rate constants and concentrations of the reactant in the feed solution.

A number of assumptions are required for the method to be mathematically justified:

(i) The composition in each vessel is uniform throughout.

(ii) The rate of change of the variable considered will be the same in a continuous flow system as in a batch vessel when the value of the variable is the same in both vessels.

(iii) The variable considered (say COD) is monotonic with respect to time.

(iv) The variable considered must have additive properties. If several volume fractions, each with different COD concentrations, are added together, then the resulting COD concentration will be the weighted average of the mixed fractions.

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If these assumptions can be applied, then the following formula has been shown to be valid:

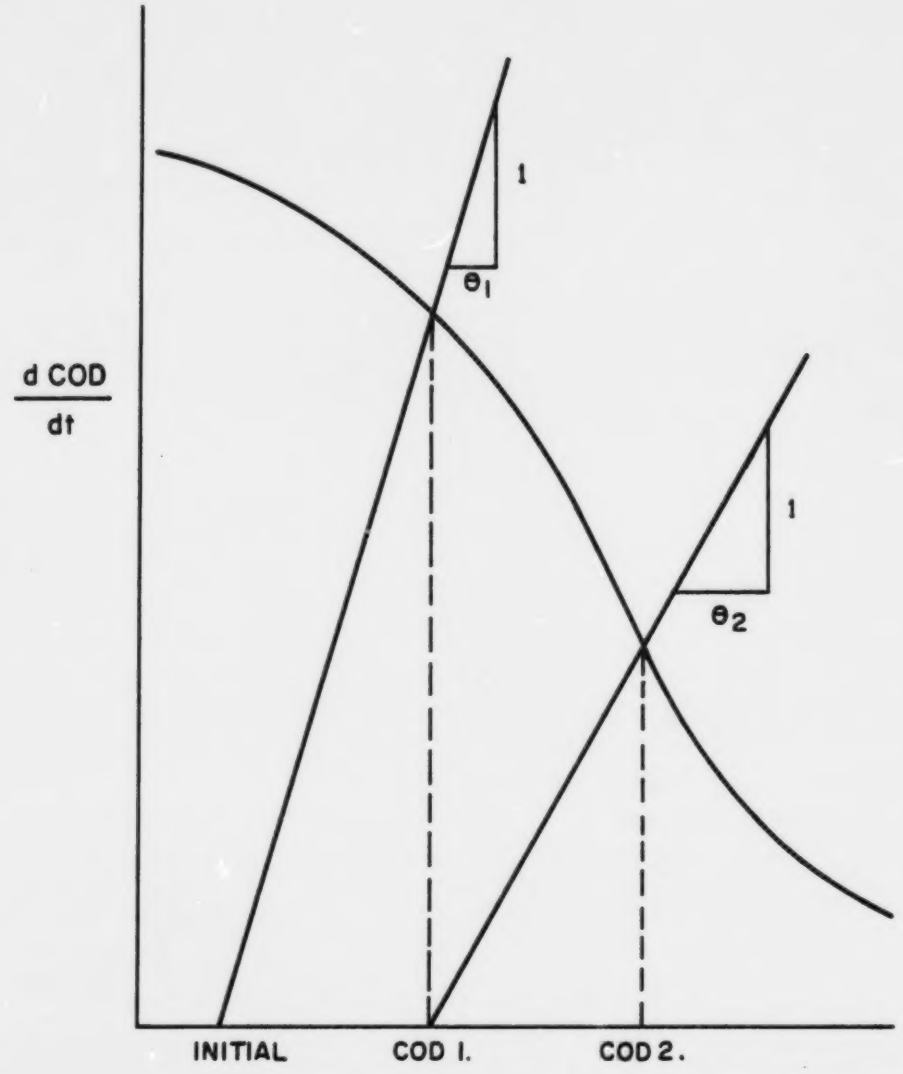
$$D_n = 1 - \frac{1}{(1 + K\theta_n)^n}$$

where: Dn = degree of completion of a reaction in the nth vessel
K = reaction velocity constant ($time^{-1}$)
θ = nominal residence time in the nth vessel (time)

For a graphical solution, the rate of change of the variable, dCOD/dt, is plotted against the variable, COD concentration. A line is then drawn from the X-axis (COD concentration) starting at the feed concentration to the vessel and with a slope equal to $1/\theta$ so that the curve is intersected. A vertical line is drawn down from the intersection point until it meets the X-axis. This point indicates the concentration of the variable at the exit from the vessel or the feed concentration to the next vessel in series. Refer to Figure 4.8 which illustrates the procedure.

The Jones method was programmed on a H.P. Model 9830 computer and used to predict continuous flow results at 232°C (450°F) from the batch data. The kinetic rate constants for the first and second reaction regimes respectively were 0.13 per minute and 0.013 per minute with the rate change at 8 minutes. A three compartment reactor was assumed with residence times corresponding to those achievable in the Wetox pilot plant, 12 minutes in the first compartment and 8 minutes each in the second and third compartments.

Actual pilot plant results at 232°C with three reactor residence times corresponded closely to those predicted from the batch kinetic data and Jones analysis. Predicted values are 60%, 67% and 70% TCOD reduction after 12, 20 and 28 minutes respectively, compared to the pilot plant results of 62%, 65% and 70% COD reduction for the same residence times. As found in the batch tests, most of the oxidation occurred during the first ten minutes of the reaction. After this transition point, there was only a very slow increase in the overall COD reduction.



- θ_1 and θ_2 ARE RESIDENCE TIMES IN THE FIRST & SECOND VESSELS
- COD 1. and COD 2. ARE EFFLUENT COD CONCENTRATIONS FROM THE FIRST AND SECOND VESSELS.

FIGURE 4·8 JONES PLOT ANALYSIS

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Copper catalyst appeared to have some advantage at both the 200 and 400 ppm levels. The rate of COD reduction improved; however, the experiments were run without excess oxygen. Therefore, the full extent of the potential catalytic effects were probably not achieved. Residence times could be somewhat reduced with the use of a catalyst, but not sufficiently to warrant the extra process complexity. There was no evidence that ultimate COD reduction could be increased with a catalyst.

Maximum feed concentration was limited to ∿ 10% macerated peat solids. More concentrated suspensions were too viscous to be pumped by the progressive cavity pump installed in the pilot plant. It also appears that the maximum oxygen transfer capability of the stirrers installed in the pilot plant was reached at approximately 8% COD (5.7% solids) concentration, even when pure oxygen or 60:40 O_2:N_2 was injected. The oxygen transfer limitation may be overcome by improved stirrer design; however, the maximum pumpable concentration of 10% solids is unlikely to be improved upon.

From these results, it is evident that wet oxidation of peat for energy recovery is technically feasible. However, the economic viability of such a process will be dependent on the specific process conditions, plant location and prices and availability of competing energy sources. Refer to the sections on plant design and economic evaluation for a detailed analysis of various alternate methods for energy recovery from peat by integrating wet oxidation of peat with other unit operations.

4.5 Corrosion Tests

The materials of which the wet oxidation plant is constructed have a strong influence on the capital costs of the process equipment. We can draw upon the operating experience of Zimmermann process plants oxidizing sewage sludge to predict what may be expected in the course of wet oxidizing peat. In addition, we have carried out corrosion tests in the Wetox pilot plant reactor.

Oettinger and Fontana (1976) reported the resistance of several alloys to wet air oxidation, including AISI types 304 and 316 stainless steels, Hastelloy Alloy C-276, Inconel Alloy 625 and titanium alloys at 177-280°C, 350 to 500 mg/L chloride concentrations in sewage sludge. Data from more than 30 sewage treatment plants show that, in over 5 years of continuous operation at pH 5 to 8, Types 304 and 316 stainless steels have excellent resistance to stress corrosion cracking at chloride concentrations up to 350 mg/L. Only Hastelloy Alloy C-276, Inconel Alloy 625 and titanium resist stress cracking when chloride concentrations exceed 400 mg/L. When chlorides are 3000 mg/L, titanium was most resistant of the materials tested. Their laboratory test and experience data correlated well at concentrations, temperatures and pH levels reported.

By comparison, peat wet oxidation proceeds at temperatures up to 270°C and pH 3-4. Chloride levels in all of our peat samples were below 50 mg/L. In the absence of high chloride concentrations and in an oxidizing atmosphere, it is reasonable to expect 304 and 316 stainless steels to withstand the action of organic acids at the acidic pH values prevailing in the peat Wetox reactors.

In the corrosion test carried out during pilot plant experiments, five test specimens were attached to the agitator blades in the first compartment of the 36-litre Wetox reactor. The test metals were titanium, Hastelloy C-276, Hastelloy G, Avesta alloy 254 SMO and 316 stainless steel. It was found that, after 42 hours of operation, there was no perceptible weight loss in the samples, so no accurate corrosion rate can be established. Microscopic examination of the specimens showed some erosion on both Hastelloy samples. The remaining specimens remained largely untouched.

Although more extensive testing will be necessary prior to constructing a peat wet oxidation plant, it is reasonable to base cost estimates on the assumption that the plant would be constructed of 316 stainless steel. Further saving would be possible if the plant could be constructed of 304 stainless steel.

5. TASK 3 - PARTIAL WET OXIDATION OF PEAT

5.1 General

The process concept investigated by these experiments aims at the production of solid peat fuel by an autothermal wet carbonization process. In order to avoid heat exchanger fouling problems which have obstructed previous attempts at commercial scale wet carbonization, a portion (∿ 10-20%) of the peat is oxidized in the Wetox(R)/wet carbonization reactor to generate just sufficient heat to maintain the reaction. Subsequently, the remaining peat solids can be dewatered mechanically.

In these experiments, the reactor conditions will be determined which result in dewaterable (to < 50% MC) peat solids. Additional data will be collected regarding solids recovery and solubilization. The results of batch experiments will be confirmed in scaled-up, continuous flow experiments in the pilot plant. The results obtained will form the basis of a process simulation, leading to the evaluation of production economics.

5.2 Experimental Methods

5.2.1 Peat Samples

Batch and continuous flow experiments have all been carried out with Northern Ontario peat. Its characteristics are described in Section 4.2.1. The preparation of the samples prior to experimentation is described in Section 4.2.2.

5.2.2 Analytical Methods

The analytical methods described in Section 4.2.3 have been used to evaluate partial oxidation experiments.

5.2.3 Equipment and Technique

Batch experiments of partial oxidation were carried out in a 2-litre stirred autoclave. It is constructed of titanium and it can withstand pressures up to 13.8 MPa (2000 psig). Temperature control was accomplished by means of external electrical heating coils for

preheating and an internal cooling coil to remove heat from the combustion reactions. The internal reactor temperature was measured by a thermocouple, which was connected to the heater controls and a continuous chart recorder. The reactor was stirred at 800 RPM by two six-bladed turbine impellers mounted on a single shaft. The layout of the autoclave is shown schematically in Figure 4.1. It is identical with that used for total oxidation experiments, except that the sample injection system was not used.

Partial oxidation was studied at temperatures between 163 and 204°C. Oxygen dosage ranged from 0 to 25% of COD charged.

For these experiments, 1 litre of raw, non-homogenized peat was loaded into the reactor. After sealing the reactor, the temperature was raised at the rate of ∿ 5.5°C/minute with slow (100 RPM) stirring to the desired level. At the desired temperature, oxygen was added at the prescribed dose and stirring was increased to 800 RPM. This was taken as time zero. After the required time, the autoclave was cooled, the pressure released and the reaction-mass sampled and dewatered.

The dewatering test was designed to approximate the processes occurring in a belt-press such as the one manufactured by Sulzer Brothers. Although no rigorous scale-up is possible from these tests, they are useful to compare the effects of various treatments among themselves.

The reacted mass, containing about 9.3% solids, was vacuum filtered in a Buchner funnel over nylon cloth. The filtered sludge generally contained 25% solids. 50 grams of this sludge was placed into a 5 cm diameter cylindrical cartridge with a porous sintered metal disk on the bottom and a close-fitting movable piston bearing down on the top of the charge. The cartridge was placed in the Carver hydraulic press and the pressure increased to 3.3 MPa over one minute. The pressure was held at this value for another minute, then released and the pressed cake removed for analysis.

Continuous flow experiments have been performed in the 36-litre pilot plant, described in Section 4.2.4.2. The experimental technique was identical with total oxidation processing, except for the reduced quantity of air injected into the stirred compartments. Dewaterability of the product was tested in the laboratory as described above.

5.3 Results

5.3.1 Batch Experiments

In the course of partial oxidation experiments, a portion of the stoichiometric oxygen demand of the peat was supplied to the peat slurry to achieve partial oxidation and the liberation of heat.

The experiments were initially carried out in a 2-litre stirred autoclave to determine the effective range of parameters which were then investigated in a 36-litre continuous flow Wetox pilot plant reactor.

The independent variables were investigated at the following levels:

- at 163°C: 9.6, 12.6, 15.7, 20, 25% stoichiometric oxygen
- at 177°C: 0, 15, 20% oxygen, and
- at 204°C: 20% oxygen dose based on TCOD charges.

The reaction time was varied from 0 to 40 minutes at the chosen temperature. The concentration of raw peat charged was held constant at 14.7% TCOD and only one kind of peat, from Northern Ontario, was subjected to experiments.

It was of interest to observe the effect of the above variables on:

- the degree of oxidation achieved
- amount of COD solubilized
- the moisture content of peat after dewatering
- the fuel value of the treated material
- recovery of heating value with treated material.

The experimental results are shown in Appendix C. Selected values were plotted in Figures 5.1 to 5.3, and are discussed below:

5.3.1.1 Extent of Partial Oxidation

The degree of oxidation of peat is determined by measuring the TCOD decline after reaction with various amounts of oxygen supplied to the reactor. The oxygen dose is expressed as the percentage of the total COD of the peat. It was anticipated that, in the stirred reactor, the oxygen would react with the peat more or less completely and liberate an amount of heat equivalent to the COD consumed.

From the data plotted in Figures 5.1 and 5.2, it is evident that the expected complete utilization of oxygen did not take place in the autoclave. There is a decline amounting to about 15% of TCOD even in the presence of a nitrogen atmosphere. This is attributed to the loss of incompletely oxidized volatile products, and possibly the formation of compounds refractory to oxidation by the reagents of the COD test.

The amount of oxygen consumed in partial oxidation, however, can be determined by a mass balance of oxygen at the pilot plant scale and this will be discussed in Section 5.3.2.

The data do indicate that the extent of the reactions increases with increasing temperature. Increasing oxygen dose shows no trend in the TCOD. The reactions appear to be complete after 10 minutes.

5.3.1.2 Solids Recovery

The solubilization of peat in the course of partial oxidation is a concern, since soluble solids and COD are not captured by the solids separation stage of the process and are lost for the recovery of solid fuel. For this reason, solubilization needs to be minimized, provided adequate treatment can be attained to achieve satisfactory dewatering of the peat. The solubilized material is subjected to anaerobic digestion in the wastewater treatment section and a portion of the chemical energy is recovered in the form of methane gas, and used as fuel to further dry the solid product.

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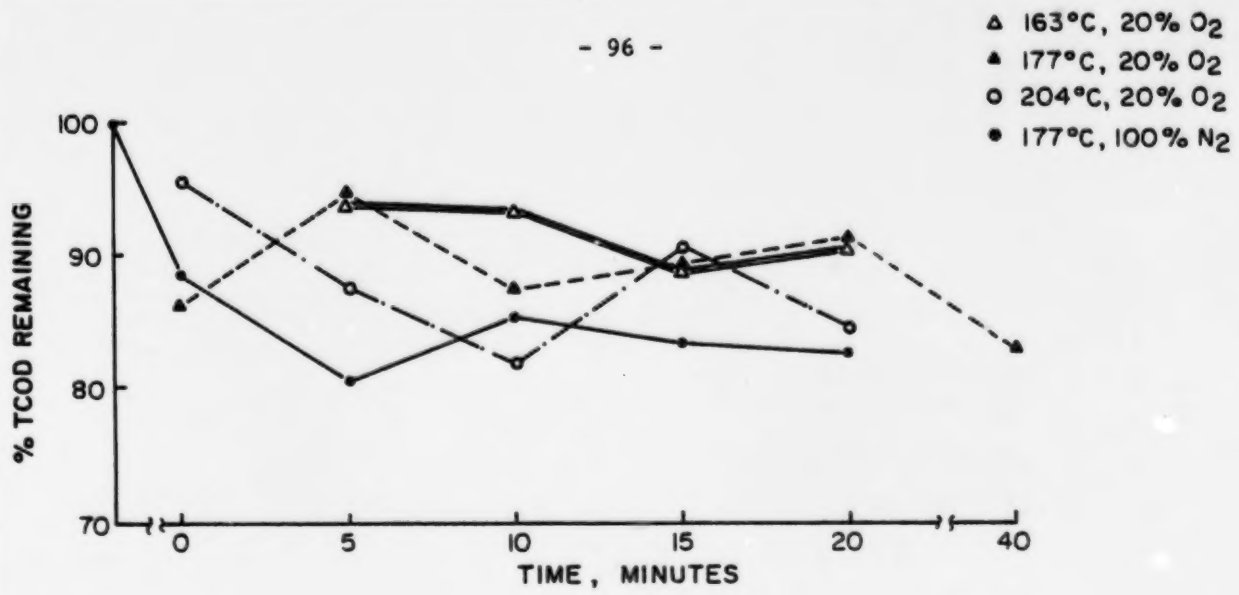

FIGURE 5.1 PARTIAL OXIDATION. CHANGE OF TCOD WITH TIME

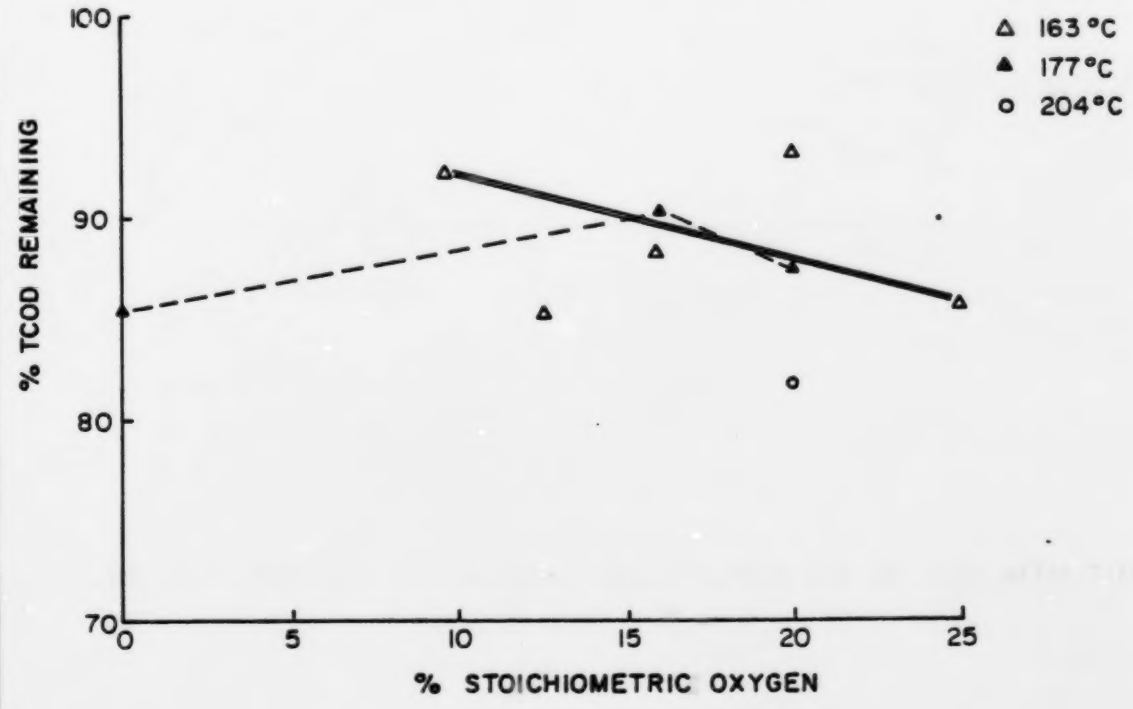

FIGURE 5.2 PARTIAL OXIDATION. CHANGE OF TCOD WITH O_2 DOSE, 10 MINS.

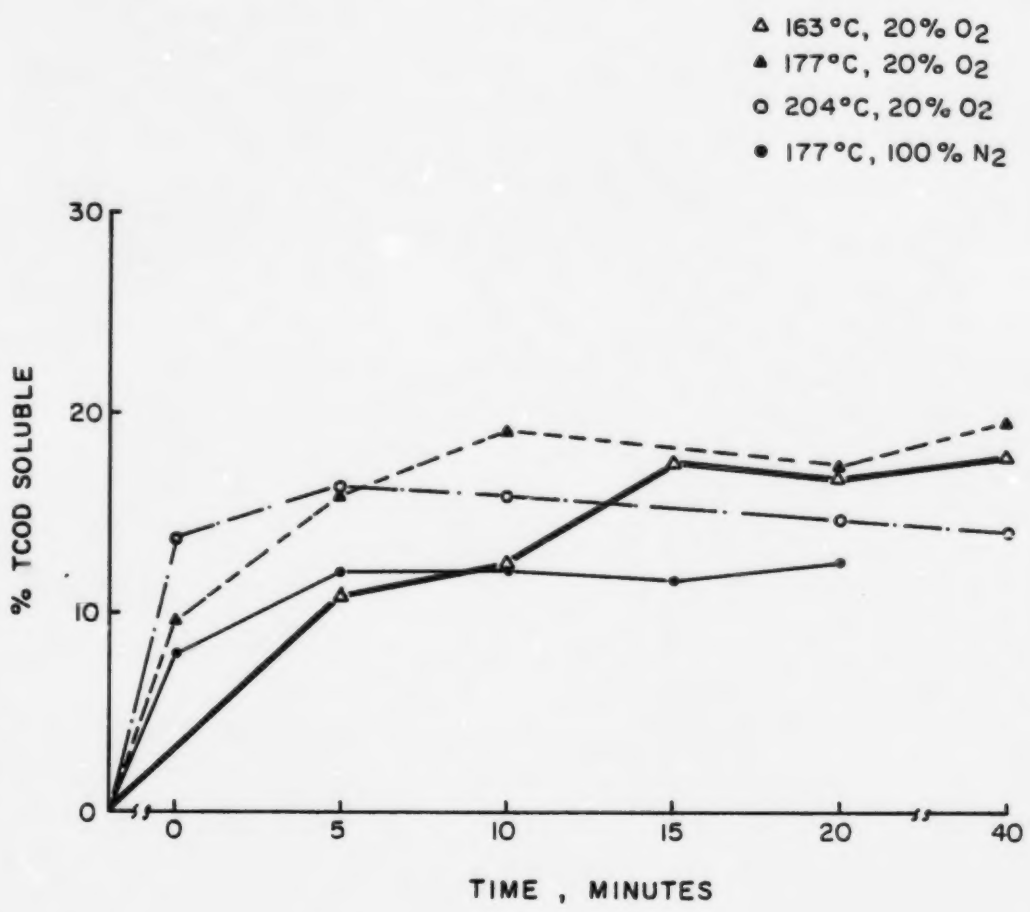

FIGURE 5.3 PARTIAL OXIDATION. SOLUBILIZATION OF COD WITH TIME.

The suspended solids recovery is expressed as the percentage of feed total solids recovered on the filter. The untreated, raw peat contains only a minute amount of filterable solids and soluble COD: dissolved solids are about 0.3% of TS and soluble COD is about 0.14% of TCOD.

Figure 5.3 shows the solubilization of COD with reaction time. It is evident that, in the presence of oxygen, more solubilization occurs. A significant amount of solubilization occurs during heat-up, but there is little change after 10 minutes' reaction. Less soluble COD is recovered at 204°C than at lower temperatures; the soluble material may be oxidizing at this temperature.

In Figure 5.4, suspended solids recovery is plotted against reaction time. The greatest solids loss occurs at 177°C, followed by values at 204°C and 163°C.

5.3.1.3 Dewaterability

The true functional test of the success or failure of the wet carbonization reaction is the dewaterability of the peat sample by mechanical pressure to less than 50% moisture conent.

Vacuum filtration without pressing yielded > 70% residual moisture in the treated samples. Pressed cake moisture versus reaction conditions is shown in Figure 5.5 Treatment at 163°C did not yield a combustible product (> 50% MC). At higher temperatures, adequate dewaterability is shown after 5 minutes (+ heat-up) residence time. The presence of oxygen provides a minor improvement of dewaterability. However, a nitrogen atmosphere will also provide satisfactory dewaterability. It is evident that the effect of thermal treatment provides the major improvement in dewaterability.

5.3.1.4 Enhancement of Product Heating Value

When aqueous peat slurries are heated, a variety of thermal reactions take place, leading to loss of carbon dioxide and water from the solids. This leads to an increase in heating

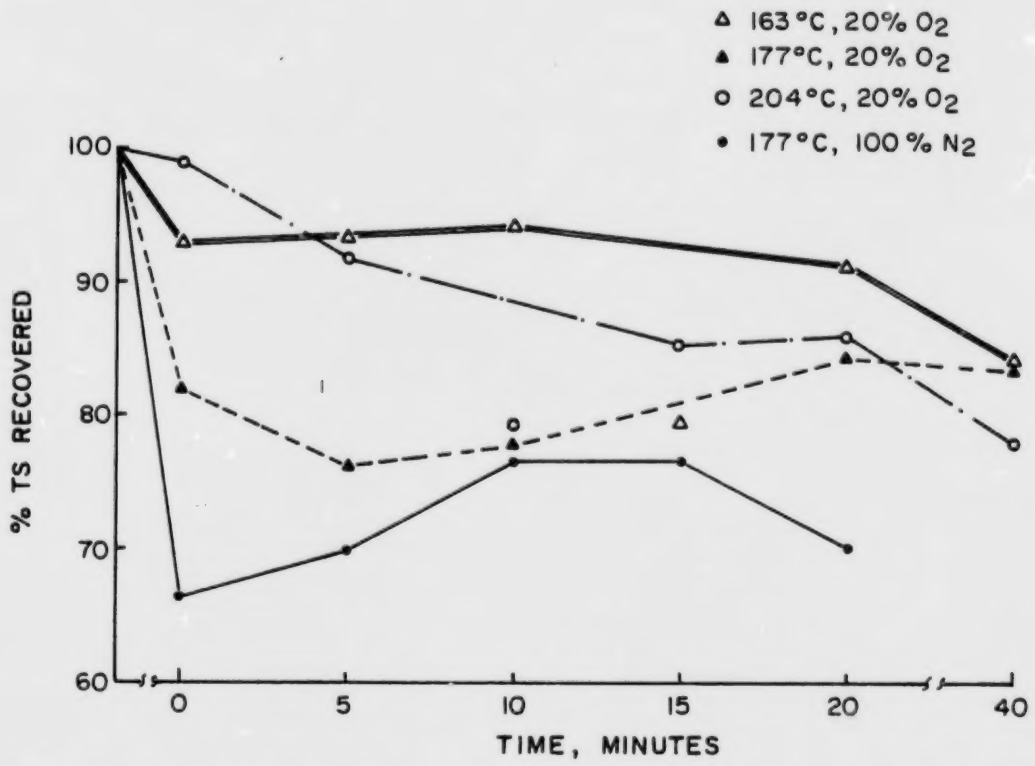

FIGURE 5.4 PARTIAL OXIDATION. SOLIDS RECOVERY vs REACTION TIME

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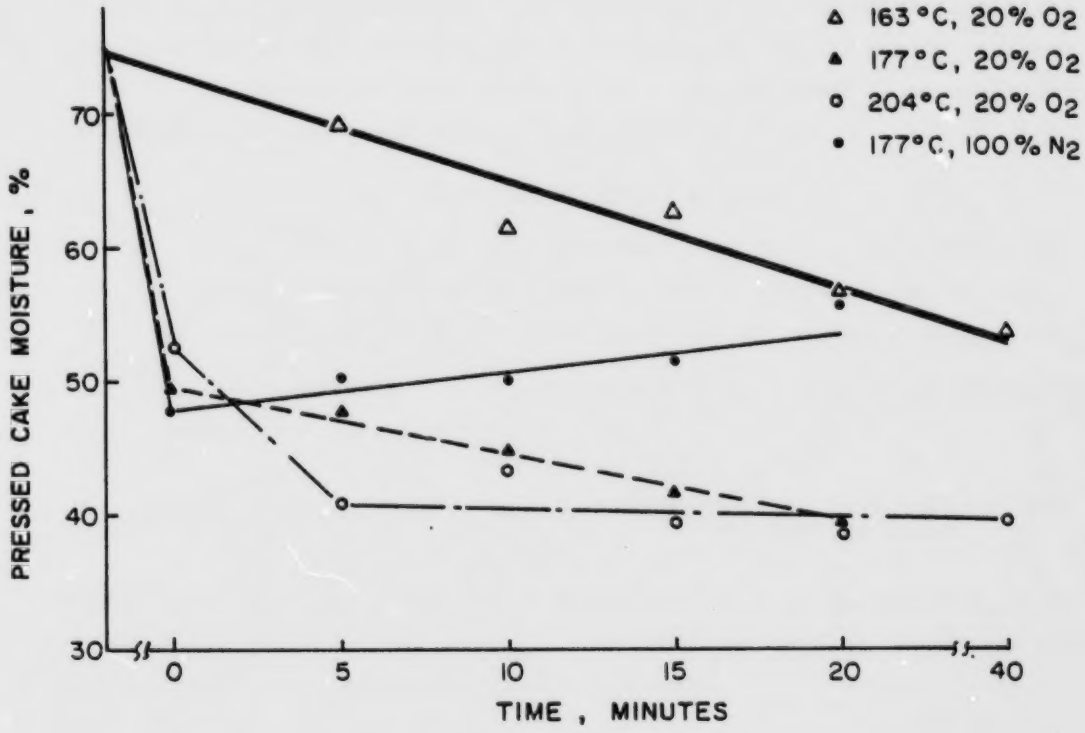

FIGURE 5.5 PARTIAL OXIDATION.
DEWATERABILITY vs REACTION TIME

value. Increases of between 5 and 32% have been reported, as a function of peat type, reaction temperature and duration (IGT, 1981). Our data, Figure 5.6, show increases of solid heating values, which decline with the duration of the reaction. With increasing oxygen tension, the net increase is diminished (see Figure 5.7). Little trend is apparent with increases in temperature for a fixed oxygen tension.

5.3.1.5 Recovery of Heating Value

The ultimate test for bringing into focus the various dependent variables discussed above is the amount of the original calorific value of the peat which can be recovered after reaction.

Therefore, the following expression was devised and the results were plotted on Figure 5.8

$$\text{Feed Heating Value Recovered, \%} = \frac{\text{Reacted Heating Value x SS Recovery}}{\text{Feed Heating Value}} \times 100$$

Since there is a net increase in ash content of the reacted material which dilutes its calorific value, gross moisture-free heating values are used in the calculation to provide a realistic picture.

In Figure 5.8, most of the values for fuel yield lie between 75 and 80%. This arises because more of the solids are recovered when oxygen is present, even though the net calorific value of the solids collected in the absence of partial oxidation is higher.

Experimentally, the solids were recovered by vacuum filtration on glass fibre filters and then dried in an oven. Recoveries in production scale equipment may be different.

5.3.2 Continuous Flow Experiments

An experiment was performed to investigate the partial oxidation of peat in the continuous flow pilot plant. The reactor was operated at 177°C and 204°C, temperatures found to be effective in batch experiments, to minimize solubilization of the peat, while achieving

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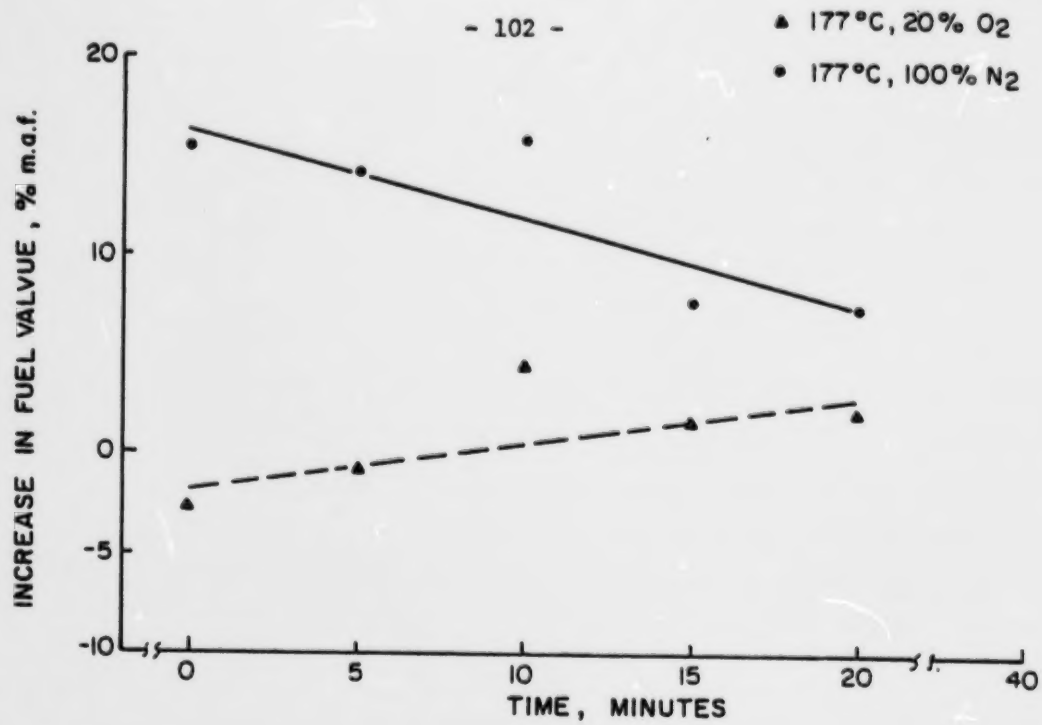

FIGURE 5.6 PARTIAL OXIDATION.
ENHANCEMENT OF FUEL VALUE vs REACTION TIME

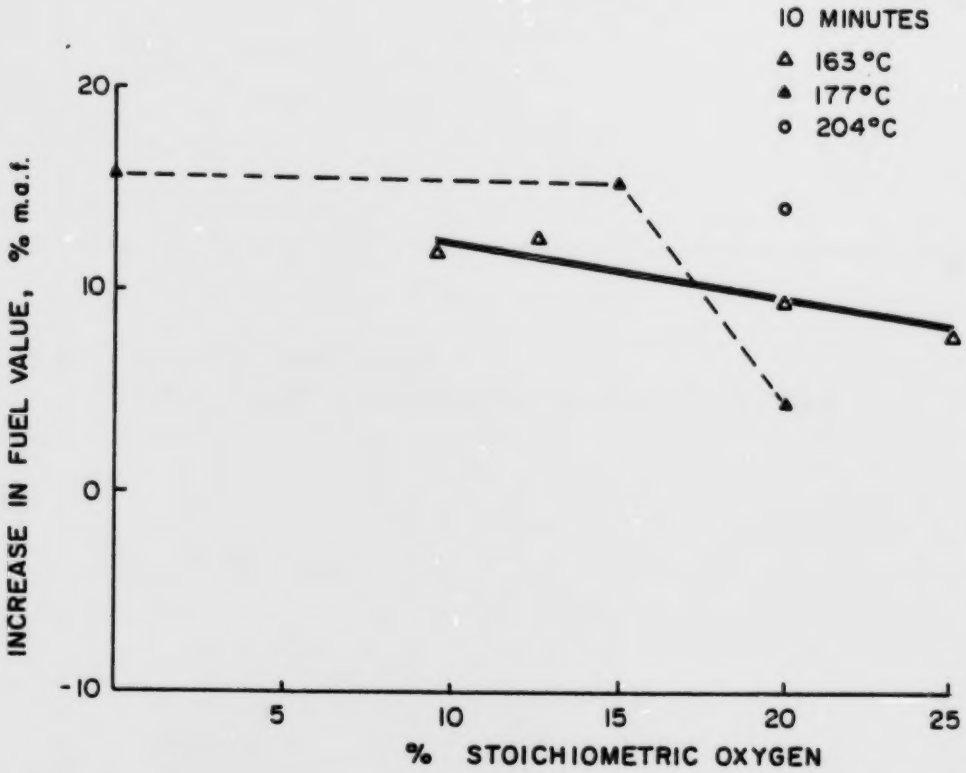

FIGURE 5.7 PARTIAL OXIDATION
ENHANCEMENT OF FUEL VALUE vs O_2 DOSE

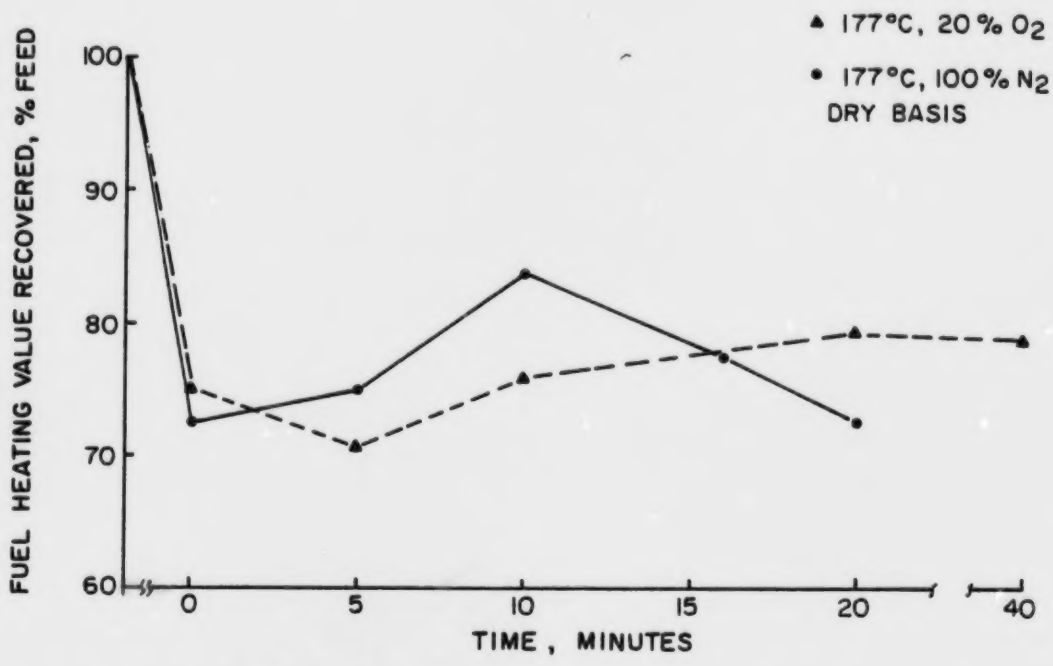

FIGURE 5.8 PARTIAL OXIDATION.
FUEL VALUE RECOVERED vs REACTION TIME

sufficient oxidation to allow autothermal operation. The effluent streams were subsequently analyzed to determine the extent of both the COD reduction and solids loss due to solubilization and combustion. The remaining solids were subjected to dewatering tests: vacuum filtration followed by hydraulic pressing as described in Section 5.2.3. Overall solids recoveries and associated heating values were determined for the continuous partial oxidation/dewatering of peat at two reaction temperatures.

The experimental conditions and results are presented in Tables 5.1 and 5.2. Only one reactor compartment was utilized to provide a ten minute hydraulic residence time with a flow of 1.2 L/min of raw peat at 6.1% solids concentration. Compressed air was used as the source of oxygen.

From Table 5.2, the effects of the reaction temperature on partial wet oxidation are evident. Increasing the temperature from 177°C to 204°C increases TCOD reduction from 17% to 27% in ten minutes. There is a corresponding increase in the loss of solids, from a 14.5% reduction to a 26.4% reduction at the higher temperature. Effluent SCOD was slightly lower at 204°C than at 177°C, indicating some oxidation of the soluble organic material.

Sufficient oxygen was supplied to permit combustion of only about 20% of the feed TCOD. In the absence of excess oxygen, considerable TCOD reduction still occurred without oxygen utilization. Of the overall TCOD reductions, approximately one half can be attributed to combustion, while other reactions, probably the loss of volatiles, account for the remaining TCOD reduction. Table 5.2 and Figures 5.9 and 5.10 present the overall mass balance for peat solids for an integrated process at the two reaction temperatures.

After wet oxidation in the pilot plant, the liquid effluent was vacuum filtered in a Buchner funnel. Although the resulting filter cakes are similar in solids concentrations, 25.7% and 24.9% for the low and high temperature reactions respectively, the filterability of the

TABLE 5.1 - Continuous Partial Oxidation Results

Reaction Temperature (°C)	177	204
Residence Time (min)	10	10
Raw Peat		
Flow (L/min)	1.2	1.2
TCOD (g/L)	96	96
SCOD (g/L)	0.15	0.15
TS (%)	6.1	6.1
Liquid Phase Effluent		
Flow (L/min)	1.06	1.06
TCOD (g/L)	89	77.7
SCOD (g/L)	15.4	13.4
TS (%)	5.9	5.1
Vapour Phase Effluent		
Flow (L/min)	0.14	0.14
TCOD (g/L)	9.5	9.5
SCOD (g/L)	9.5	9.5
TS (%)	0.01	0.01
Overall Reductions		
TCOD (%)	16.9	27.4
TS (%)	14.5	26.4
Air Supply (scfm)	2.3	2.3
Oxygen Used (g/min)	9.1	12.4
COD Red./O_2 Used (g/g)	2.14	2.55

TABLE 5.2 - Solids Recovery and Dewatering Results from Continuous Partial Oxidation

Reaction Temperature (°C)	177	204
Raw Peat		
Dry Heating Value (MJ/kg)	20.2	20.2
Flow (L/min)	1.20	1.20
TS (g/L)	6.1	6.1
(g/min)	73.2	73.2
Liquid Phase Effluent		
Flow (L/min)	1.06	1.06
TS (g/L)	5.9	5.1
(g/min)	62.5	54.1
Vacuum Filtration		
Sludge TS (%)	25.7	24.7
Filtrate TS (%)	1.1	0.93
Volume (%)	80.5	82.5
Net Solids Recovery (g/min)	53.1	46.0
(% of total)	72.5	62.8
Hydraulic Pressing at 3.3 MPa		
Sludge TS (%)	35.2	48.8
Pressate TS (%)	1.2	1.0
Volume (%)	28	50
Overall Solids Recovery (g/min)	52.4	45.1
(% of total)	71.6	61.6
Heating Value (MJ/dry kg)	20.9	21.8
Net Recovery (% of total)	74	66

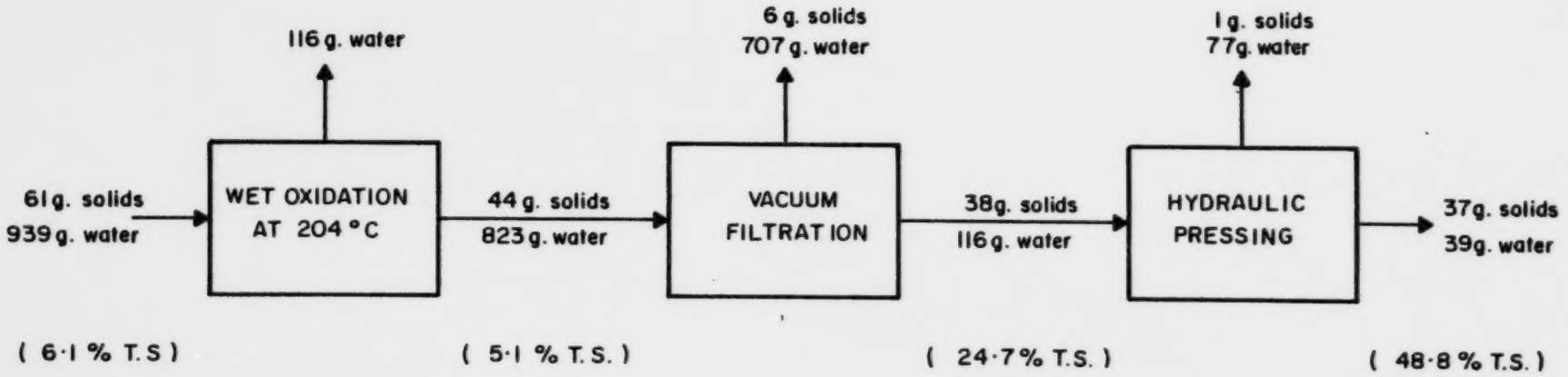

FIGURE 5.9 MASS BALANCE FOR PARTIAL WET OXIDATION AT 204°C FOLLOWED BY TWO STAGE SOLIDS DEWATERING.

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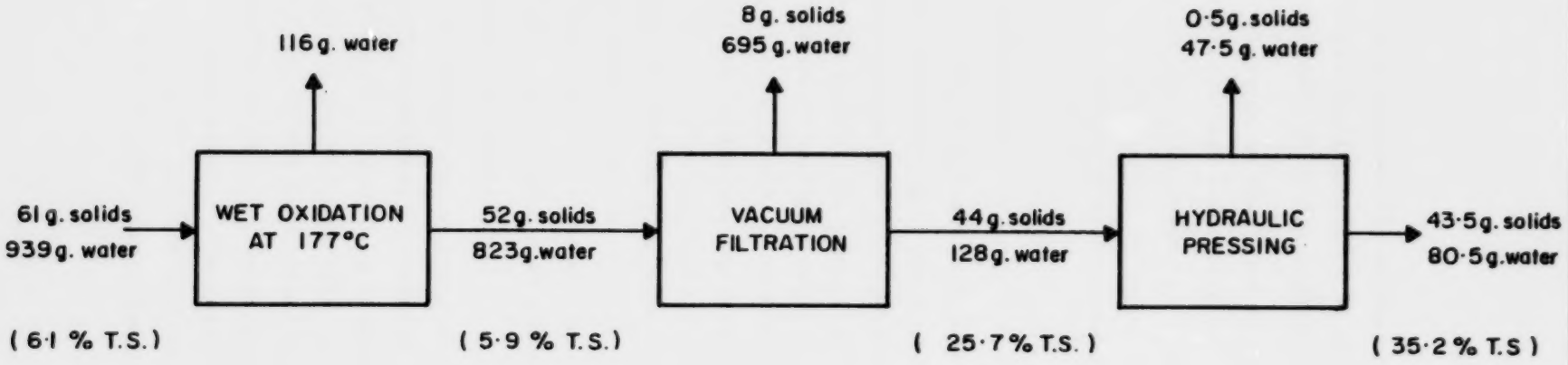

FIGURE 5.10 MASS BALANCE FOR PARTIAL WET OXIDATION AT 177°C FOLLOWED BY TWO STAGE SOLIDS DEWATERING.

effluents were considerably different. Filtration of one litre of the 177°C effluent required almost 30 minutes compared to the effluent produced at 204°C which filtered in about one minute.

Although at the lower reaction temperature a higher percentage of the treated solids are recovered, these solids cannot be mechanically dewatered to the target value of ∿ 50% solids. Therefore, the 204°C reaction temperature will be chosen for plant design. This value is comparable to the temperatures used in wet carbonization (192-200°C) by others.

5.4 Discussion

It has been known from previously published work (Mensinger, 1980) that, upon heating to above 163°C, peat slurries undergo irreversible changes which allow them to be dewatered by the application of pressure to less than 50% moisture content. This is the wet carbonization reaction, which is currently nearing commercialization in a process devised by B. Myreen (Rohrer, 1980). The heart of the process is a pressure reactor, in which the wet carbonization reaction is carried out at 200°C. Although this reaction is slightly exothermic, the generated heat is insufficient to achieve this temperature without the injection of externally generated steam and additional elaborate efforts must be made to recover heat from the processed slurry. The heat recovery is complicated by the thick, viscous nature of the peat slurry and its tendency to foul heat exchanger surfaces.

To obviate the problems of heat exchange, Cederquist and Berring (1952) suggested the concept of autogenetic wet carbonization, in which the peat is preheated by direct injection of steam flashed from the reactor and the reacting mass is further heated by partial oxidation of the peat in the wet carbonization reactor. They carried out continuous-flow pilot plant experiments, the results of which have been reported in their paper. The details of the reaction were not reported in sufficient detail to allow the reactor design to be duplicated. Therefore, this work was undertaken to confirm and expand their work.

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In the batch mode of experimentation, various reaction conditions were investigated ranging from 163 to 204°C, oxygen dosages between 0 and 25% stoichiometric ratio to TCOD and reaction times from 0 to 40 minutes' residence times. Homogenized Northern Ontario peat was used for these experiments at the single feed concentration of 9.3% total solids; the material forms a pumpable slurry at this solids concentration. The parameters measured after reaction were the degree of oxidation achieved, amount of fuel solubilized (as expressed by soluble COD), the effectiveness of mechanical dewatering and the amount of fuel value recovered in the remaining solids. These experiments served to obtain experimental conditions for the subsequent continuous flow pilot plant scale processing.

Based on the bench-scale tests reported in Section 5.3.1, it was concluded that, in the pilot plant, a minimum temperature of 177°C will be tested, with the expectation that 204°C would give a greater degree of oxidation and heat production. A minimum treatment time of 10 minutes was also prescribed.

The results of continuous flow experiments indicated that, at 204°C and after ten minutes, the peat solids have been sufficiently carbonized to allow mechanical dewatering to about 50% moisture content, with overall solids recovery at about 62% of the initial feed. Although almost 40% of the solids have been solubilized or lost, TCOD reduction has only been 27%. Considerable potential energy will be available from the liquid effluent streams in the form of both sensible heat and soluble COD. The anaerobic digestion (see Section 6.4) of Wetox effluent indicated about 75% removal of the solubilized COD to be feasible, resulting in 2.9 x 10^{-3} m^3 of methane produced for every 76 g of pressed cake at 48.8% moisture content. The energy available from burning the methane will be used to fuel a rotary drum dryer which has been incorporated into the plant design (Section 7.4.4.2). Computer analysis of the process model showed that sufficient gas is generated to achieve 32-33% moisture in the final product (Section 8.2.3).

In order to satisfy both the energy requirements of the process and to minimize capital costs, it is desirable for the process to be autothermal. This requires the oxidation of a certain fraction of the raw peat to be used to maintain the reaction temperature, to provide sufficient heat for preheating the raw peat slurry, and for further thermal drying of the final peat cake. In order to prevent a need for sophisticated heat exchangers to overcome high temperature fouling, direct steam injection into the raw peat slurry is the preferred method for preheating. This requires a specific quantity and quality of steam, depending on the preheating requirements.

If heat is recovered from both the liquid and vapour effluent streams by generating steam in a waste-heat boiler, this clean steam directly injected in the feed stream will provide adequate preheating and will eliminate the problem of fouling heat exchangers. This was the approach taken in the partial oxidation plant design (Section 7.3).

The specific operating conditions and the associated heat balance and costs are investigated in detail in the sections on plant design and economic evaluation.

6. TASK 4 - WASTEWATER TREATMENT AND BIOGAS GENERATION

6.1 General

The wet-mined peat enters the processing plant at 90 to 97% moisture content. Practically all of this water will have to be disposed of, most conveniently by returning it to the bog where it originated. Both total and partial wet combustion will leave the wastewaters with significant amounts of dissolved contaminants: whatever amount of COD is not burned or recovered as solid product will appear in the effluent. The exact amounts depend on process conditions, and will be calculated in the process design case studies of Section 7.4.

The dissolved residues consist largely of simple organic acids, which could be good substrates for anaerobic digestion. Anaerobic treatment would not only reduce the waste load in the effluent, but it would improve the energy balance of the plant by generating biogas (a mixture of methane and carbon dioxide), which can be burned for energy recovery. Prior to discharge into the environment, the anaerobically digested effluent must be treated in a conventional activated sludge (aerobic) process, which reduces the effluent BOD_5 concentration to an acceptable level.

As it will be shown in the plant design, Section 7.4, the wastewater treatment process very significantly contributes to the energy economy of total or partial peat wet oxidation plants.

Both treatment processes examined here are carried out by microbial cultures in suitable vessels. The experimental approach used will establish the response of an anaerobic filter to the wet oxidized peat wastewater. Then, we shall prorate the projected cost and performance of an advanced anaerobic reactor configuration (Van den Berg, 1982), and incorporate it into the plant designs.

6.2 Experimental

6.2.1 Analytical Techniques

Most of the analytical techniques employed in this Section have been referenced in Section 4.2.3.

Nitrate and nitrite determinations were performed on a Dionex Ion Chromatograph operated according to recommended practice.

Gas analysis was performed using gas chromatography. The column used was made of 9 feet of 1/8" stainless steel tubing filled with 100/120 mesh Carbosieve B. This allowed quantitative determination of all gases present except nitrogen, which was calculated by difference. A thermal conductivity detector was used on the instrument.

6.2.2 Anaerobic Treatment of Wetox Process Effluent

6.2.2.1 Column Construction

Two Plexiglass cylinders, each having a length of 135.3 cm and a diameter of 10.2 cm, were employed for the construction of the bench-scale anaerobic digesters. The process design selected was that of a horizontal packed bed reactor. Raschig rings, of approximately 1.5 cm in length, were obtained from the Metals, Glass and Ceramics Department, ORF, for use as support media for the biological film which develops in the reactor. The rings used in Tube #1 were composed of 94% shale and 6% grog, while those in #2 were cordierite.

The columns were subdivided into sections of approximately 30.5 cm in length, using perforated baffles. These baffles were designed to allow unobstructed fluid flow between compartments but prevented gas transfer. Two sampling ports were installed in each subdivision: one for gas collection and the other for liquid collection. Gas samples were collected in gas sampling bags.

In order to maintain the internal column temperature at 37.5°C (in the mesophilic range), fifty feet of 1/4" flexible copper pipe was wrapped around each column. The copper pipe was then connected to a recirculating, thermostatically controlled water bath, adjusted to maintain an internal column temperature of 37.5°C. Pipe insulation was wrapped around the entire apparatus to minimize heat loss and temperature gradients.

6.2.2.2 Start-up

Anaerobic seed, obtained from Lakeview Sewage Treatment Plant, was drained into the two nitrogen filled columns. The seed was transferred into the columns under a nitrogen atmosphere. During

operation, precautions were taken to minimize contacting the culture with air. The units were started on wet oxidized peat liquor. To allow acclimatization of the culture, the loading rates were kept low. The longitudinal design of the columns allowed for the different waste strengths delivered to each section to be determined separately.

6.2.2.3 Operation

Prior to preparing the feed, it was necessary to settle the two constituents in order to remove the carbonaceous ash sediment from the liquid phase and the peat wax from the vapour phase. Jar tests showed that the use of commercial flocculants did not improve the settling of the char and, therefore, it was allowed to sediment without chemical aid. The vapour phase condensate was passed through a #1 Whatman filter using vacuum filtration in order to separate the wax.

After settling, the two phases were mixed in a ratio of two parts LPE (liquid phase effluent) to one part VPC (vapour phase condensate). The resulting mixture was neutralized to pH 6.5 using $NaHCO_3$. The use of this chemical provided a degree of buffering capacity to the reactor contents in the event of an upset.

To ensure that sufficient nitrogen and phosphorus levels for proper cell growth were available, the feed was analyzed. Nitrogen determinations included ammonia, total kjeldahl nitrogen, nitrate and nitrite. Total phosphorus was also determined. A 20 element scan on a DC-Plasma Spectrophotometer was performed to obtain the concentrations of heavy metals in the feed. Heavy metals did not exist in toxic amounts (Tables 4.9, 4.10). Phosphorus measurements demonstrated that the concentration of this nutrient was too low to assure proper biological growth. Additional phosphorus was provided in the form of K_2HPO_4 at a concentration of 1 g per litre.

In order to determine column efficiencies, weekly analyses of suspended solids, volatile suspended solids, pH, and chemical oxygen demand were performed on the feed and effluents. BOD_5 and BOD_{10} analyses were performed on the feeds and effluents at periodic intervals throughout the course of the study.

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To minimize blockage that might occur in the feed lines the prepared feed was decanted. Chemical toxicity or overloading can cause very rapid reactor upset. As a precaution, Unit #1 was run on feed which was diluted 1:4 with water. Two separate peristaltic pumps provided control over the hydraulic retention time of each column. Unit #1, with the dilute feed, received 2078 mL/day giving a hydraulic retention time of 2.4 days. Unit #2 received 594 mL/day of full strength waste, for a retention time of 8.8 days. The resulting effluent was saved for further treatment in an aerobic system.

The quantity and composition of the gas produced indicates the internal condition of the biological reactors. Gas analysis was performed using gas chromatography.

6.2.3 Aerobic Treatment of Anaerobic Digestion Effluent

6.2.3.1 Aerating Chamber Construction

Aerobic treatment was modelled by an activated sludge system comprising two chambers: the first is required for aeration and mixing and the second is employed for settling. The aeration chamber is approximately 27 L in volume. Aeration is achieved by means of a plastic air diffuser which can be positioned in order to obtain the most effective mixing of the contents. The settling chamber is approximately 13 L in volume. It is separated from the aeration chamber by a series of baffles. These baffles serve to prevent mixing of the sludge and to facilitate the return of settled sludge to the aeration chamber. Settled liquor is allowed to drain over a fixed partition and can be collected or vented to drain at this point. Feeding is performed on a continuous basis using a peristaltic pump.

6.2.3.2 Start-up

Settled sludge was obtained from Oakville Sewage Treatment Plant. Twenty-five litres of sludge were placed in each of two units and the remainder of the volume was made up with water. Suspended solids, volatile suspended solids, pH, chemical oxygen demand,

dissolved oxygen and dissolved oxygen uptake rate measurements were performed in order to determine the condition of the seed. The mixed liquor volatile suspended solids level (MLVSS) was adjusted to 300 mg/L at the start. Airflow was adjusted to maintain adequate mixing. It was desirable to keep a dissolved oxygen concentration of 6.0 - 6.5 ppm, although this was not always possible due to problems with sludge bulking.

6.2.3.3 Operation

Effluent from each of the two anaerobic units was treated in the same manner: pH was adjusted to 7 using 10% H_2SO_4, and the effluents were decanted to remove any solids. Feed was delivered at a rate of 3500 mL/day. At this level, the hydraulic retention time was 7.7 days for the mixed section, and 11.4 days for the entire system. Both aerobic units were analyzed for the aforementioned parameters on every second day. Sludge was washed from the settling chamber as necessary to maintain MLVSS at about 3000 mg/L. Biological oxygen demand (BOD) measurements were made at given intervals for both the feed solution and the effluent.

6.3 Results

6.3.1 Anaerobic Digestion

Two horizontal anaerobic filters were initially fed full strength wet oxidized peat supernatant at hydraulic retention time of 8.8 days. Full strength trials with Unit #1 were terminated on March 5, 1982, after a period of worsening performance, as measured by COD removal. It was reseeded with municipal digester sludge and started up on a feed of diluted Wetox$^{(R)}$ supernatant. Figures 6.1 and 6.2 trace the performance of Unit #1 and Unit #2 respectively.

Unit #2 adapted somewhat better to the full strength substrate. It demonstrated a declining performance through February and March, which strengthened in the last month of operation to show a relatively consistent COD removal efficiency of 50%. Analyses of evolved gas collected at the end of the trial showed a methane composition ranging from 70-75%.

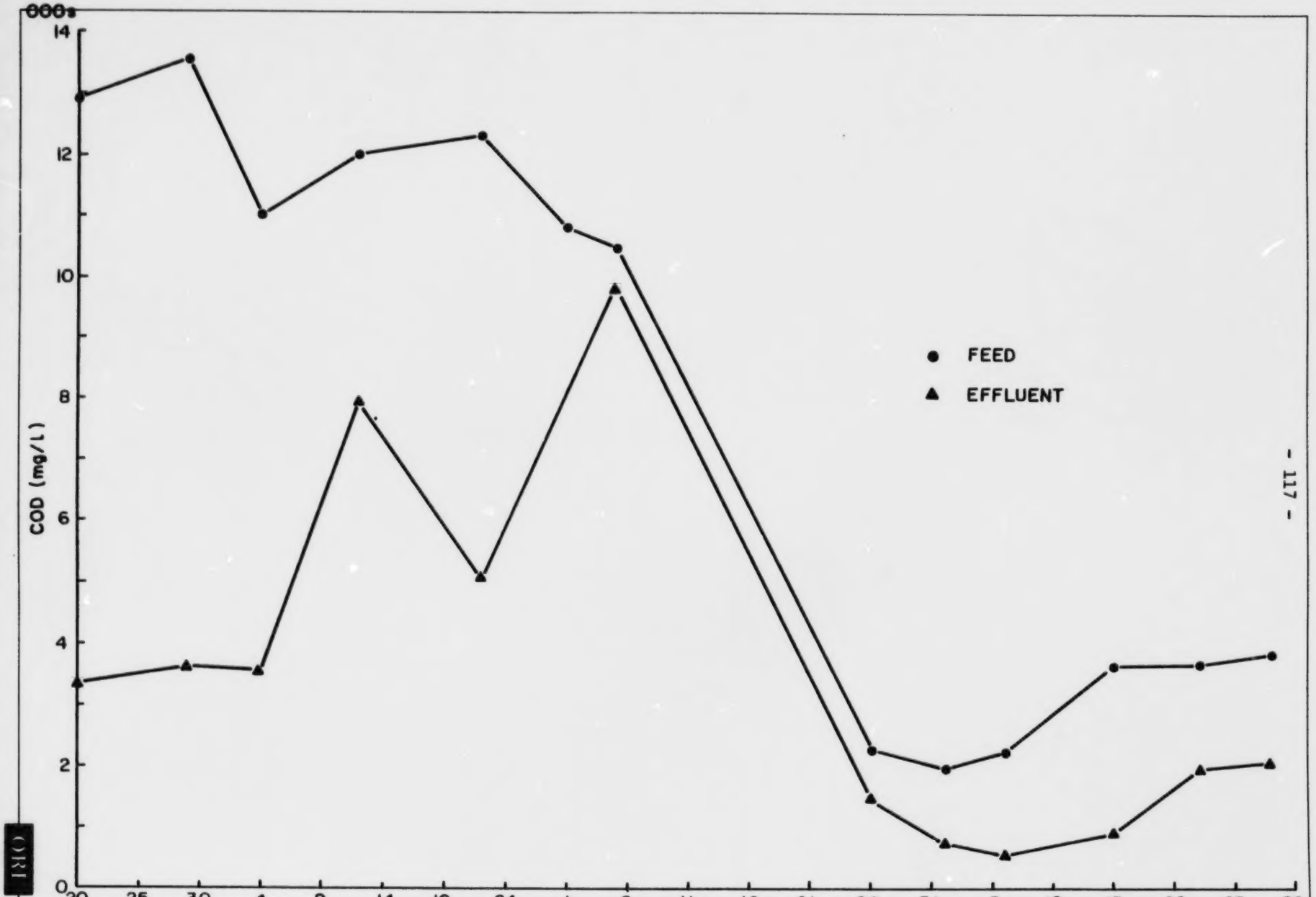

FIGURE 6·1 ANAEROBIC FILTER PERFORMANCE UNIT No.1. COD vs TIME

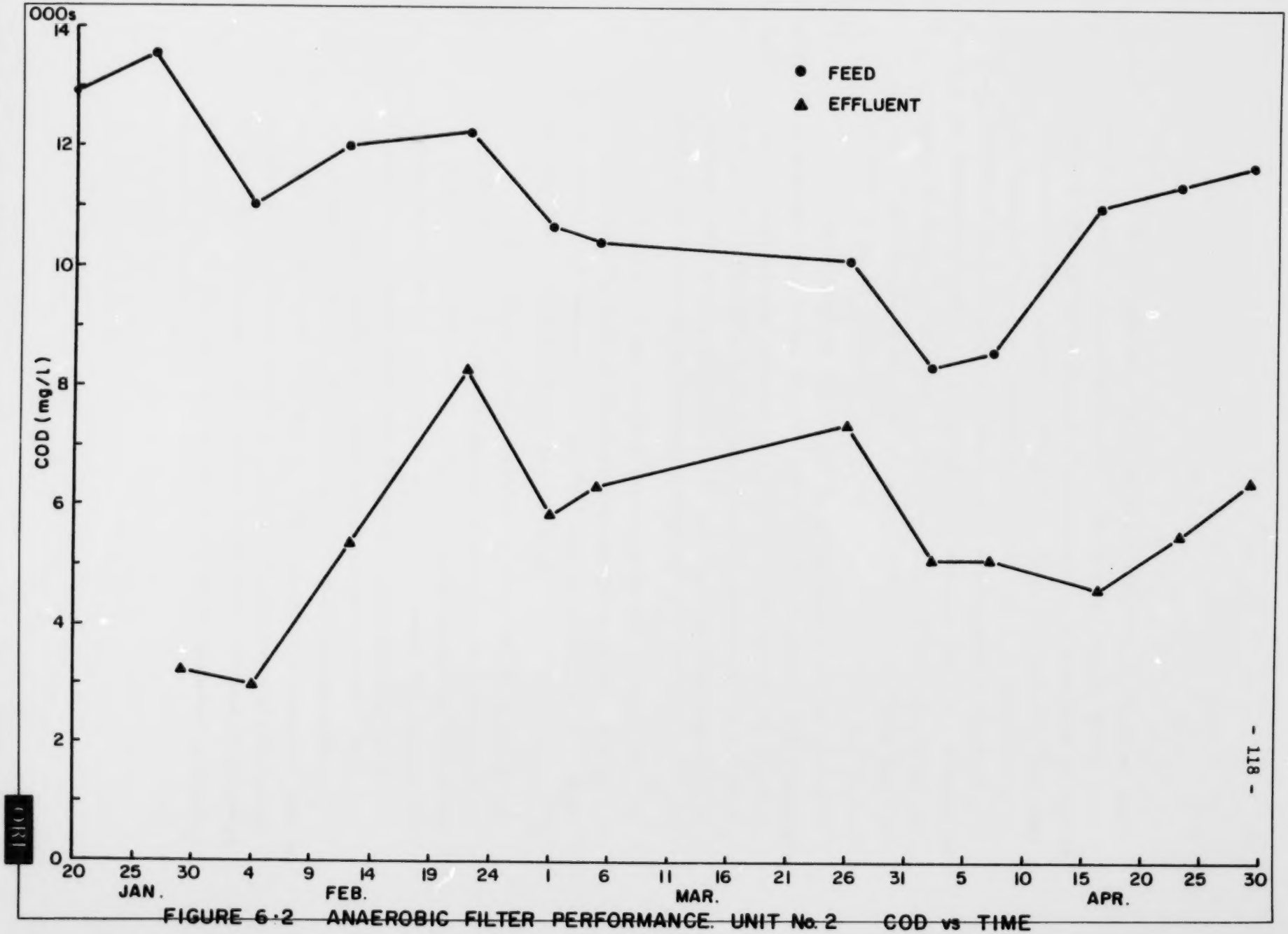

FIGURE 6·2 ANAEROBIC FILTER PERFORMANCE. UNIT No. 2 COD vs TIME

Unit #1 was reseeded on March 11, 1982, and recirculated until March 21 before feeding was started. The organic loading on the anaerobic filter was maintained at approximately the same level as Unit #2, except with a feed diluted to one quarter strength, applied at four times the hydraulic throughput (hydraulic retention time 2.43 days). COD removal efficiency improved steadily until establishing a 75% COD removal by mid-April. Table 6.1 summarizes performance on April 7. Starting on April 16, a new lot of higher strength wet-oxidized peat supernatant was fed. Table 6.3 shows the drop in removal efficiency following the step increase in organic loading.

Difficulty was experienced in maintaining a near neutral pH in both anaerobic filter units. The high ammonia content of the substrate together with lack of a strong volatile acid production within the biological system (this being largely accomplished by the wet oxidation) are the likely origins of the problem. To mitigate these difficulties, feed pH was maintained at approximately 6.5.

Figures 6.3 and 6.4 show the change in COD concentration with distance along the axis of the horizontal anaerobic units. The bulk of COD removal is accomplished in the first portion of both units. This was confirmed by observations of gas evolution.

Three regions of near steady-state operation are noted in the duration of the trials, namely, the end of April for Unit #2 and the beginning of April for Unit #1. Table 6.3 presents data on the applied loading rates, removal per volatile solids, and removal efficiencies for COD and BOD_5. Fairly consistent COD removal rates appear based on volatile solids content, as an indicator of active biomass. This calculation was performed using the mass of volatile solids added to seed each of the columns on March 11, 1982, and with the assumption that net net growth of biological solids was not significant over the intervening one and one-half months. BOD_5 removal rates show a decrease with reduced loadings. With BOD_5 and COD, the extent of removal decreased at higher loadings and concentrations.

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TABLE 6.1 - Anaerobic Filter Unit #1
Typical Results*

	April 7			April 29		
	Feed	Effluent	% Removal	Feed	Effluent	% Removal
COD	2233	554	75	3850	2079	46
BOD_5	1050	220	79	2600	760	62
TKN	220	305			188	
NH_3	140	144			165	
NO_3	3	1.3				

* Concentrations in mg/L

TABLE 6.2 - Anaerobic Filter Unit #2
Typical Results*

	April 7			April 29		
	Feed	Effluent	% Removal	Feed	Effluent	% Removal
COD	8624	5082	41	11704	6468	45
BOD_5	5200	2150	59	6900	2600	62
TKN	364	525		660	600	
NH_3	276	375		575	380	
NO_3	-			5	<1	

* Concentrations in mg/L

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TABLE 6.3 - Summary of Anaerobic Filter Performance

Unit	Period	Applied Loading Kg/m^3-day		Kg Removed Kg VSS-day		Removal Efficiency		Effluent mg/L	
		COD	BOD_5	COD	BOD_5	COD	BOD_5	COD	BOD_5
1	April 7	0.919	0.432	0.0636	0.031	75	79	554	220
1	April 29	1.58	1.06	0.067	0.07	46	62	2079	760
2	April 7	0.981	0.592	0.0371	0.032	41	58.7	5082	2150
2	April 29	1.33	0.785	0.055	0.045	45	62	6468	2600

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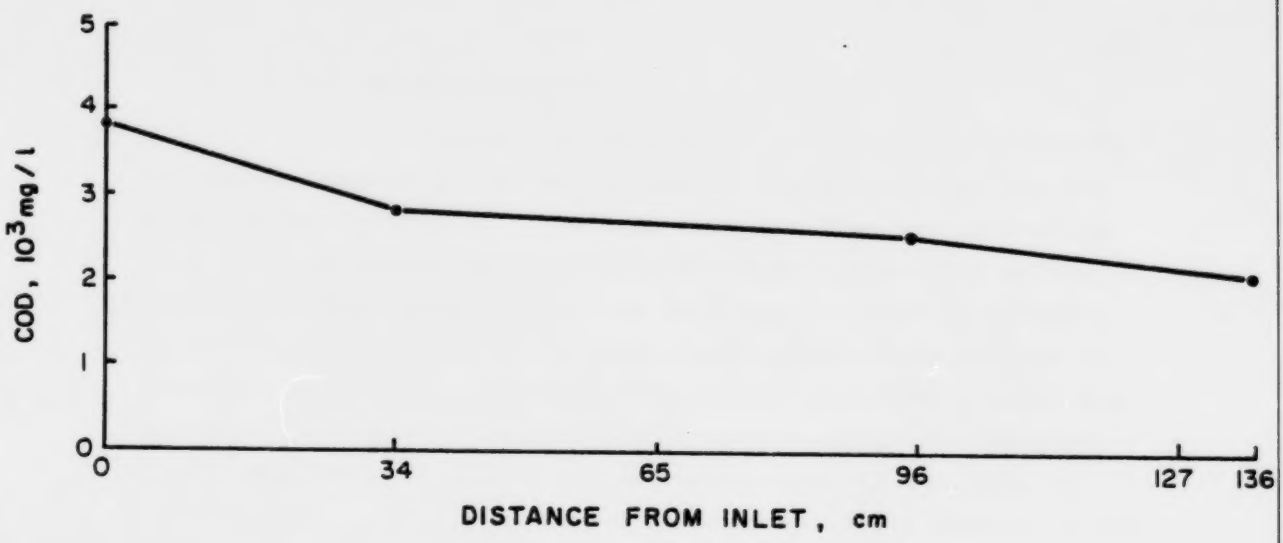

FIGURE 6·3 COD CONCENTRATION PROFILE. UNIT 1.
COD (mg/l) vs DISTANCE (cm)

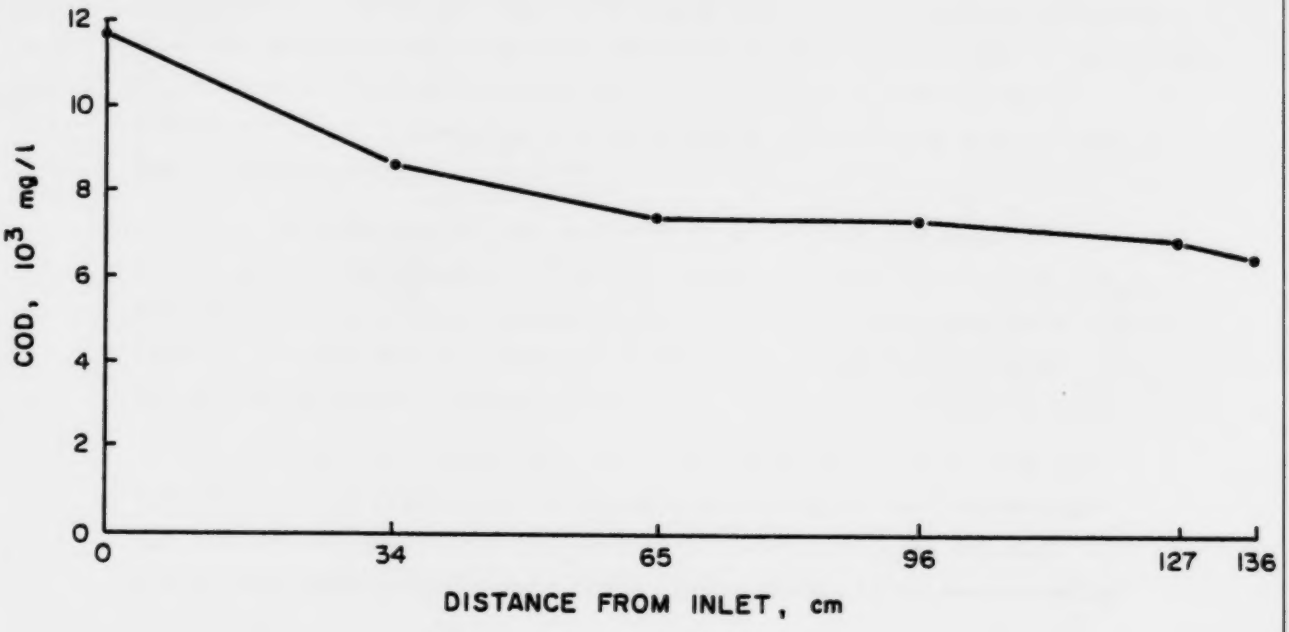

FIGURE 6·4 COD CONCENTRATION PROFILE. UNIT 2.
COD (mg/l) vs DISTANCE (cm)

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6.3.2 Aerobic Treatment

Figures 6.5 and 6.6 show influent and effluent COD for Aerobic Units #1 and #2 respectively. Figure 6.7 shows specific oxygen uptake for Unit #2. The long retention times provided by the model activated sludge units preclude meaningful information on removal efficiencies from being derived from the first few weeks of operation. It is notable, however, that specific oxygen uptake rates for Unit #2 strengthened steadily, indicating that organic constituents were being successfully oxidized. Specific oxygen uptake rates never achieved significant levels in Unit #1 due to overaeration and low levels of available BOD_5. High aeration was required to mix the contents of the tank.

Over the initial acclimation period, both units were receiving a feed which had been prepared from effluents which had been collected from the anaerobic filters prior to the start-up of the aerobic units. After April 7, 1982, the activated sludge units were receiving effluents from the anaerobic columns, with activated sludge Units #1 and #2 receiving accumulated effluents from anaerobic Units #1 and #2 respectively. Tables 6.4 and 6.5 summarize the performance of activated sludge Units #1 and #2 respectively.

Aerobic Unit #1 was operated at an average F/M ratio of 0.0156 kg BOD_5/kg VSS.day. This low loading was due to the high BOD_5 removal in the preceding anaerobic unit. The unit performed as a lightly loaded, extended aeration system, in which the mixed liquor solids concentration showed a steady decline due to endogeneous respiration.

Activated sludge Unit #2, which received effluent from the anaerobic filter treating full strength wet oxidized peat supernatant, was operated at an average F/M loading of 0.13 kg BOD_5/kg VSS.day. A high BOD_5 removal efficiency and a steady mixed liquor concentration were noted.

Activated sludge Unit #1 showed a significant degree of nitrification in spot tests. Approximately one-quarter of the nitrogen was present as nitrate in the effluent at the end of the trial period.

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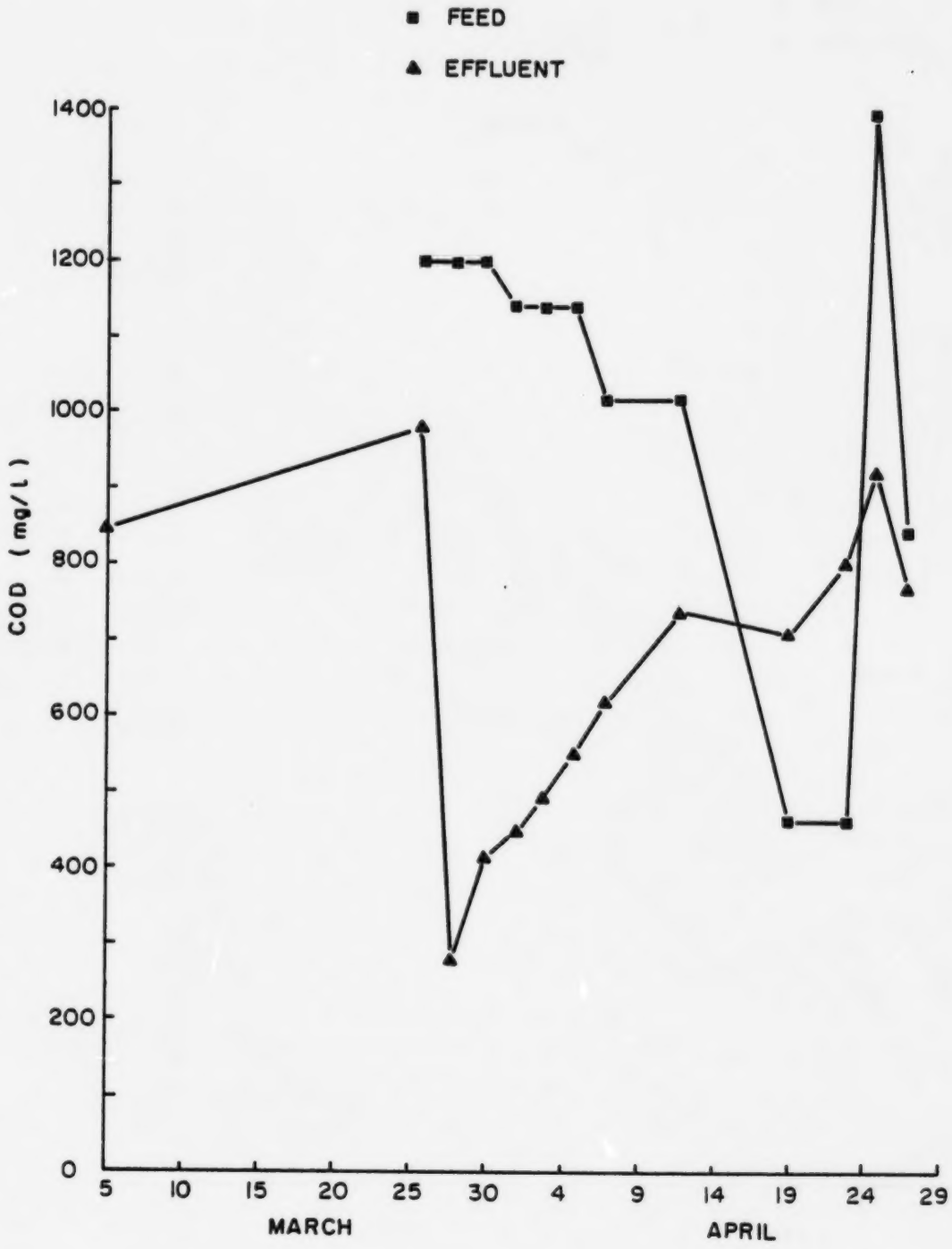

FIGURE 6-5 AEROBIC ACTIVATED SLUDGE SYSTEM. UNIT No. 1
COD vs TIME

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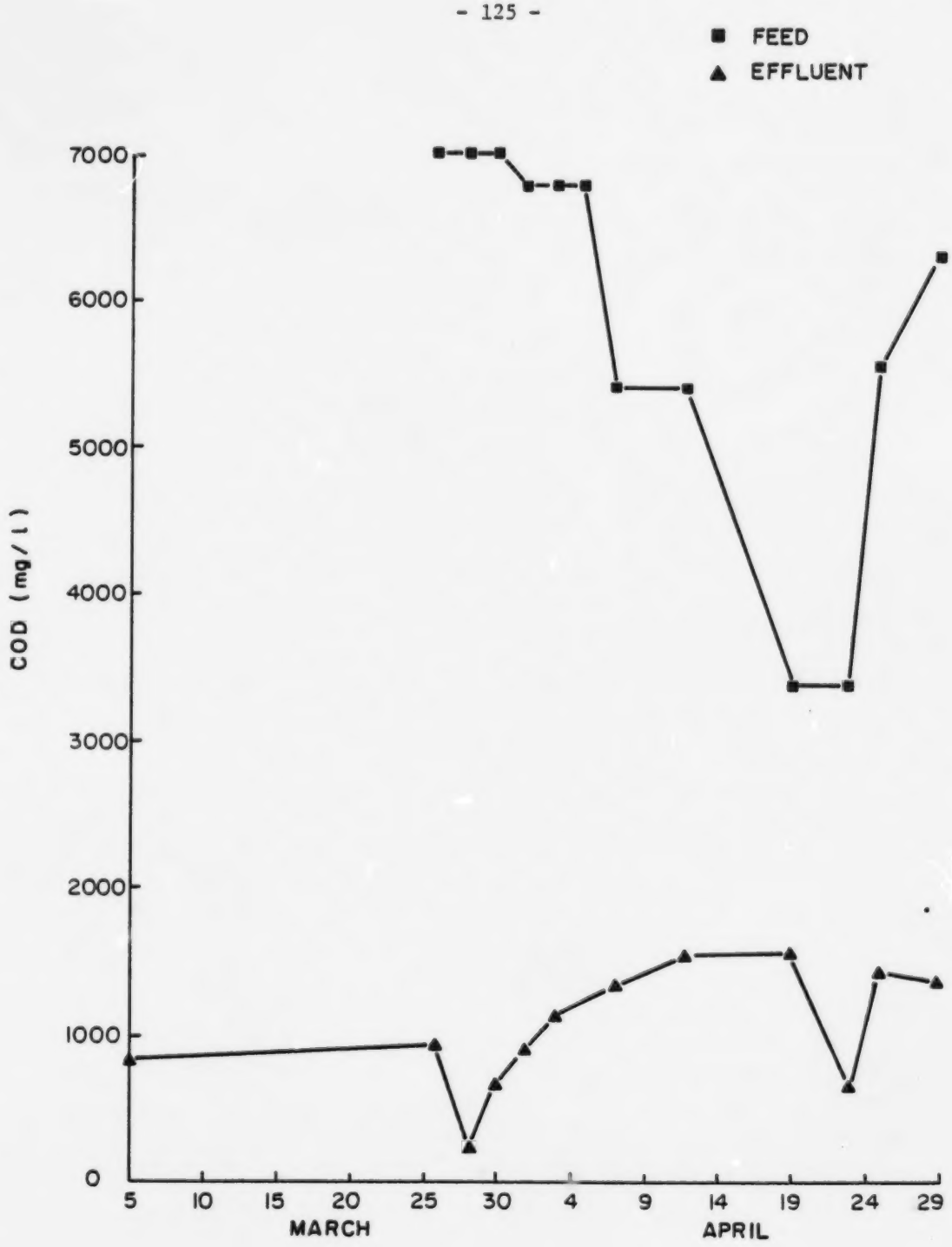

FIGURE 6·6 AEROBIC ACTIVATED SLUDGE SYSTEM. UNIT No. 2
COD vs TIME

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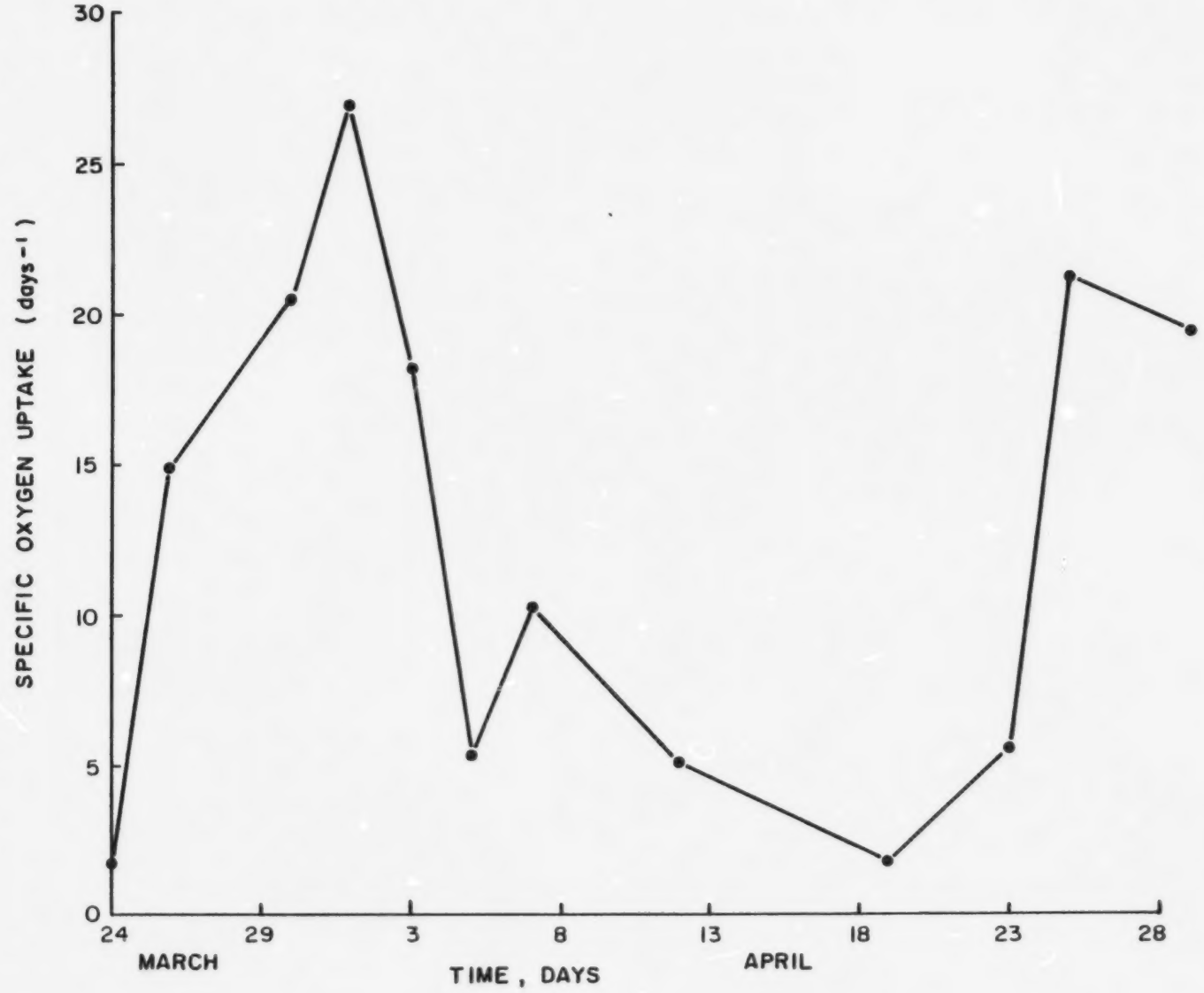

FIGURE 6·7 AEROBIC ACTIVATED SLUDGE SYSTEM. UNIT No. 2.
SPECIFIC OXYGEN UPTAKE vs TIME.

TABLE 6.4 - Activated Sludge Unit #1
Average Performance, April 7 - 29

	Influent mg/L	Mixed Liquor mg/L	Effluent mg/L	% Removal
COD	962		878	9
BOD_5	357		35	90
TSS	123	5742	145	-
VSS	97	2968	120	-

TABLE 6.5 - Activated Sludge Unit #2
Average Performance, April 7 - 29

	Influent mg/L	Mixed Liquor mg/L	Effluent mg/L	% Removal
COD	4902		1304	73
BOD_5	3290		45	98.6
TSS	472	5997	233	51
VSS	333	3215	143	57
TKN-N*	555		154	
NH_3-N*	375		95	
NO_3-N*	<1		75	

* Nitrogen values reported for April 29 only

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Operation of the aerobic units was continued after the trial period with a minimum of attention. A spot check of nitrogen levels in the aerobic unit feeds (anaerobic effluents) and aerobic unit effluents was obtained on July 8, 1982, to ascertain the degree of nitrification. The results of analyses are contained in Table 6.6.

6.4 Discussion

6.4.1 Anaerobic Digestion

Trials of anaerobic treatment of wet oxidized peat supernatant demonstrated a high level of removal of biodegradable organics. Higher removal efficiencies were recorded with more dilute input, implying a degree of inhibition of the biological processes. This inhibition is expected with the barely acclimated municipal anaerobic digester seed sludge.

High ammonia levels were recorded in the influent to the anaerobic units, in the range of 200 to 300 NH_3-N mg/L and 300 to 600 NH_3-N mg/L for Units #1 and #2 respectively. While levels of ammonia (expressed as nitrogen) of 200 to 1500 mg/L have been regarded as having no adverse effects (McCarty and McKinney, 1961), a pronounced lag-phase has been reported by some workers (van Velsen and Lettinga, 1981, and Melbinger and Donnellon, 1971) when digested sewage sludge was employed as the innoculum. These same studies have shown that, after a suitable acclimation period, ammonia-nitrogen concentrations as high as 3000 mg/L could be tolerated. According to the critical work on ammonia toxicity, the free ammonia species concentration is limiting, and, at 150 mg/L, it is toxic to methanogens (McCarty and McKinney, 1961). At a pH of 8, which was typical in the effluent from anaerobic Unit #1, the concentration of total ammonium corresponding to 150 mg/L of free ammonium-nitrogen is 1200 mg/L. At a pH of 8.8, which was typical of Unit #2, the corresponding concentration is 290 mg/L NH_3-N. This latter ammonium concentration was routinely exceeded during the trials.

At the concentrations of ammonia encountered, the problem of ammonia toxicity is essentially a problem of pH control. A degree of pH

TABLE 6.6 - Nitrification Performance of Activated Sludge Units (July 8, 1982)

	Unit #1		Unit #2	
	Feed	Effluent	Feed	Effluent
Ammonia	72	1.5	315	6.2
Nitrate	<1	211	2	550
Nitrite	<3	<3	<10	18

control was attempted during the trials by buffering and reducing the influent pH to the anaerobic filters. However, the plug flow design of the units precluded adequate control.

Removals, based upon total volume, achieved on the anaerobic filters (∿ 0.07 kg COD/kg VSS.day) were a relatively small fraction (about one-tenth) of maximum removals reported for anaerobic treatment systems (1.0 kg COD/kg VSS.day). A more liberal interpretation would increase the observed removal performance to about one-quarter of the maximum, since most of the COD removal was achieved in the first compartment of the horizontal anaerobic filters. Nethertheless, the trials demonstrated that anaerobic treatment is an effective and efficient means of removing carbonaceous wastes from wet oxidized peat supernatant. A COD removal efficiency of 75% is predicted for anaerobic treatment. An additional benefit of anaerobic treatment is the potentially valuable by-product methane gas. The concentration observed for methane in evolved gases was 70-75%, which is somewhat higher than that observed in other studies of the biogasification of peat.

The methane rich nature of the evolved gases is predictable from the high volatile acid concentration in the wet oxidized peat. The fermentation of complex organics to volatile acids typically results in the evolution of carbon dioxide, which, in this case, is partially avoided.

Maximum COD loading rates were not determined in this study. This was, in part, due to the short duration of the project. Acclimation of methanogenic cultures can require a full year to achieve ultimate COD loading rates and removal efficiencies. As noted above, ammonia toxicity is deemed to be the limiting factor governing the performance of the experimental anaerobic filters, rather than the kinetics of methanogenesis. Given the good removal efficiencies obtained by the barely acclimated units when free ammonia concentrations were within acceptable values, the wet oxidized peat supernatant is predicted to be an excellent substrate for methanogenesis if pH, and hence, free ammonia, is adequately controlled. Control of pH would necessitate mixing by recycle in the anaerobic filters, with pH monitoring and the addition of acid or base as required.

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For the purposes of the preliminary design and economics presented in Sections 7 and 8, respectively, a treatability factor of 0.8 (compared to bean blanch wastewater) and a loading rate of 12 kg COD/m^3.day are considered reasonable assumptions.

6.4.2 Aerobic Treatment

The BOD_5 contents of wet oxidized peat supernatants pretreated by anaerobic filters were effectively reduced by aerobic treatment with activated sludge systems. Activated sludge treatment at low loading rates (the units were operating in an extended aeration mode) produced no measurable excess biological sludge. Indications of partial nitrification of ammonia were recorded. While only approximately 25% of the nitrogen was converted to nitrate, it is significant that the wastewaters were not toxic to nitrifying bacteria. This also suggests that a longer period of acclimation would achieve improved ammonia conversion. In addition, trial conditions were not maintained for optimum nitrification, notably pH varied from the slightly alkaline conditions preferred by nitrifying bacteria (Culp, Wesner and Culp, 1978). A spot check of nitrification performance, conducted after the end of the formal trial period, indicated that eventually the units were able to achieve greater than 99% conversion of nitrogen from ammonia to nitrate.

Effluent quality achieved by the aerobic treatment models (see Table 6.5) demonstrated that aerobic biological treatment is able to successfully remove BOD_5 from the process wastewaters when operated under extended aeration conditions (F/M ratio of 0.13).

The experimental programme established the amenability of anaerobically digested wet oxidized peat supernatant to treatment for the removal of BOD_5 and ammonia by extended aeration. However, high nitrate levels did result from nitrification of the ammonia. Removal of nitrate could be effected by biological denitrification. It may be possible to achieve this in the anaerobic filters and thus avoid an additional step of wastewater treatment by operating the anaerobic and aerobic systems as a nitrification/denitrification process.

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An alternative scenario would be to strip ammonia from the anaerobic filter effluent and recover it subsequently. This would entail additional process steps (ammonia air stripping and acid scrubbing). However, a valuable by-product could be recovered (ammonium sulfate) and the energy input for aerobic treatment could likely be reduced from the extended aeration mode to conventional activation sludge.

A third and fourth alternative for nitrogen control are the use of ammonium specific and nitrate specific ion exchangers.

7. TASK 5 - PROCESS SIMULATION

7.1 General

The unit processes investigated in Tasks 2 through 4 are incorporated into process design case studies. The case studies are simulated mathematically with the objective of determining the capital and product costs for a range of operating conditions. Cases 1 and 2 are based on total oxidation of peat and recovery of energy, Case 3 is based on partial oxidation and recovery of a solid fuel product. Wastewater treatment is incorporated into all three case studies.

In this Task 5, the plant designs and simulation programs are devised for the three case studies. The results of the simulations are presented in the next chapter, as Task 6.

7.2 Total Oxidation: Cases 1 and 2

The heat produced from the wet oxidation of the peat is available in the form of hot water and steam at or near the reaction temperature, typically 235°C. The most economical use of this energy is highly dependent on the location of the plant and the local requirements. In this study, two alternatives have been investigated.

Case 1 assumes a direct market for the hot water, whether for space heating or for low temperature process applications. The plant design, therefore, consists of only the Wetox reactor, heat exchangers used for preheating the raw peat, high pressure feed pump, air compressor and anaerobic digestion of the effluent. Heat exchangers required for recovery of the product energy are not included in the design. The process and economic model (refer to Section 7.4) provides a cost of producing the hot water in $/GJ assuming a sink temperature of 32°C (90°F). Refer to Figure 7.1.

Case 2 is to utilize the hot water and steam for electrical generation. This has the advantage of being relatively independent of site selection since, unlike hot water, electricity is readily transported.

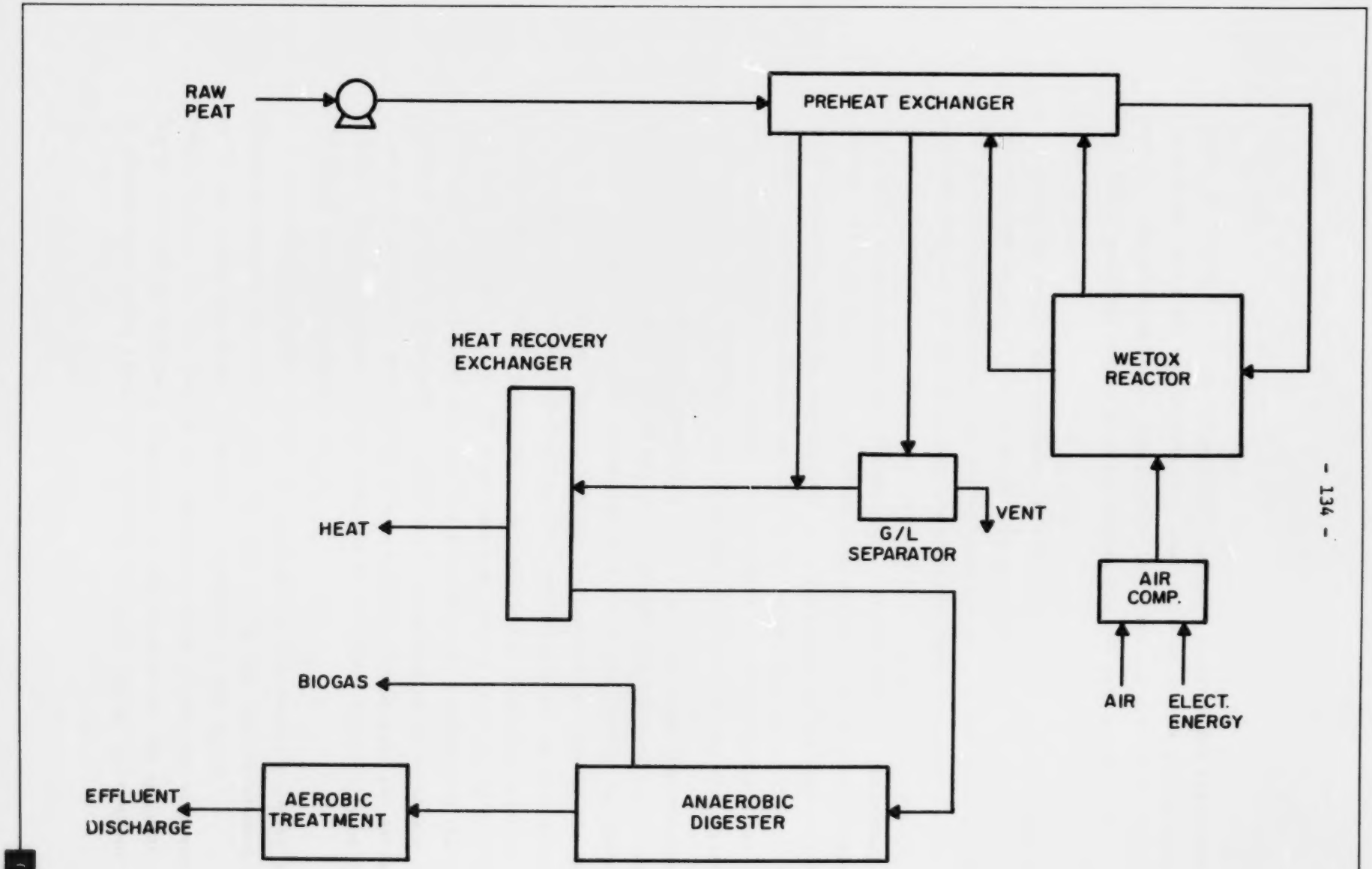

FIGURE 7·1 CASE I. WET OXIDATION OF PEAT FOR HEAT GENERATION.

Refer to Figure 7.2 which illustrates a process designed for electrical generation using the wet oxidation of peat combined with a binary steam cycle. Thermodynamically, the process is relatively efficient, since the steam condenser serves also to preheat the raw peat prior to wet oxidation.

The design and economics of the binary cycle were obtained from Schapiro and Hajela (1979) in which several power cycles were analyzed for electrical generation from geothermal sources. Brine temperatures are very similar to wet oxidation temperatures, hence the same thermodynamic considerations apply, and, because brine is generally very corrosive, binary cycles are recommended. It has not been determined whether effluent from a wet oxidation reaction could be utilized directly in a turbine. However, considering its nature (low pH and high solids content), an indirect method for generation is recommended. This particular steam-to-steam binary cycle without superheating has a net efficiency of about 13%, not including the efficiency of the wet oxidation.

Experiments with the Wetox pilot plant indicated that maximum COD reductions of 65 to 70% in the Wetox reactor are likely to be achieved. In order to improve overall conversion efficiency and, hence, the system economics, ways must be found to utilize the residual portion of the peat. Of the remaining 35% of the starting COD, essentially all is in a soluble form and can be readily converted to methane in the anaerobic digester (refer to Section 6.3.1). This methane can then be utilized to provide extra generating capacity and improved efficiency by superheating the steam produced in the binary cycle. Data on the superheating of steam and how it affects efficiency and economics were obtained from Hensler and Axtmann (1979). Final treatment of the effluent is performed aerobically before discharge to the environment.

In the analysis of the two alternative flowsheets, a number of common parameters are used. The feed rate of the raw peat is assumed to be 50 wet tonnes per hour. Therefore, depending on the solids concentration, the COD loading and subsequent power production will vary. Energy recovery by anaerobic digestion of the organics in the effluent is accomplished using fixed-film reactors utilizing design information

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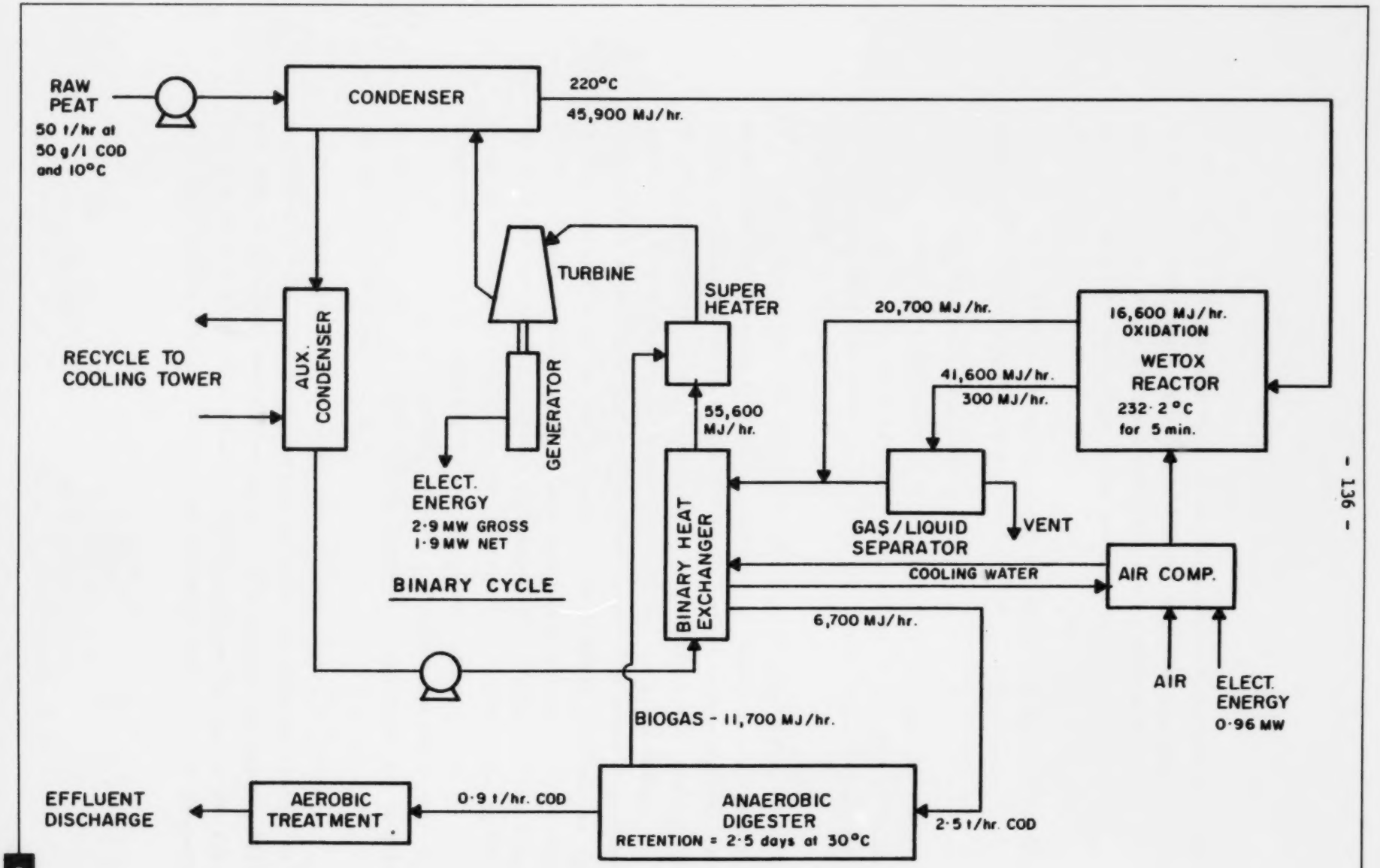

FIGURE 7.2 CASE 2. WET OXIDATION OF PEAT FOR ELECTRICAL GENERATION.

provided by Dr. B. Van den Berg of the National Research Council (1982). Although no experiments with Wetox effluent have been performed with these reactors, it is believed that the results obtained with the reactors described in Section 6.3.1 are indicative of expected performance.

More details concerning the plant design are provided in the description of the computer model, Section 7.4.

7.3 Partial Oxidation: Case 3

As an alternative to total oxidation of the peat for energy recovery, the partial oxidation/wet carbonization of the peat to enhance its dewaterability was investigated. A flow sheet illustrating Case 3 is presented in Figure 7.3

Although reaction temperatures are lower than during total oxidation, 204°C compared to 232°C, the limited amount of heat generated during the reaction necessitates preheat temperatures approaching 200°C. To avoid the use of conventional heat exchangers which are likely to be subject to severe fouling at these temperatures, the plant design incorporates steam injection into the raw peat. The steam is produced by heat exchange with the hot effluent. The effluent is likely to cause much less fouling, since it is a hot liquid and not a cold slurry (as with the raw peat) in contact with a hot metal surface. The clean steam is injected directly into the raw peat feed, thereby raising its temperature but also lowering the solids concentration. This necessitates the use of a larger reactor. However, the efficiency of the process is not affected since most of the heat is recovered and recycled in the form of more steam.

Following heat exchange, the effluent slurry is dewatered mechanically with a Sulzer belt press to about 50% moisture content as it was done in the bench scale experiment. The pressate is anaerobically digested in a fixed-film reactor to produce methane for use in the gas-fired Heil rotary drier. Capital and operating costs for the dewatering

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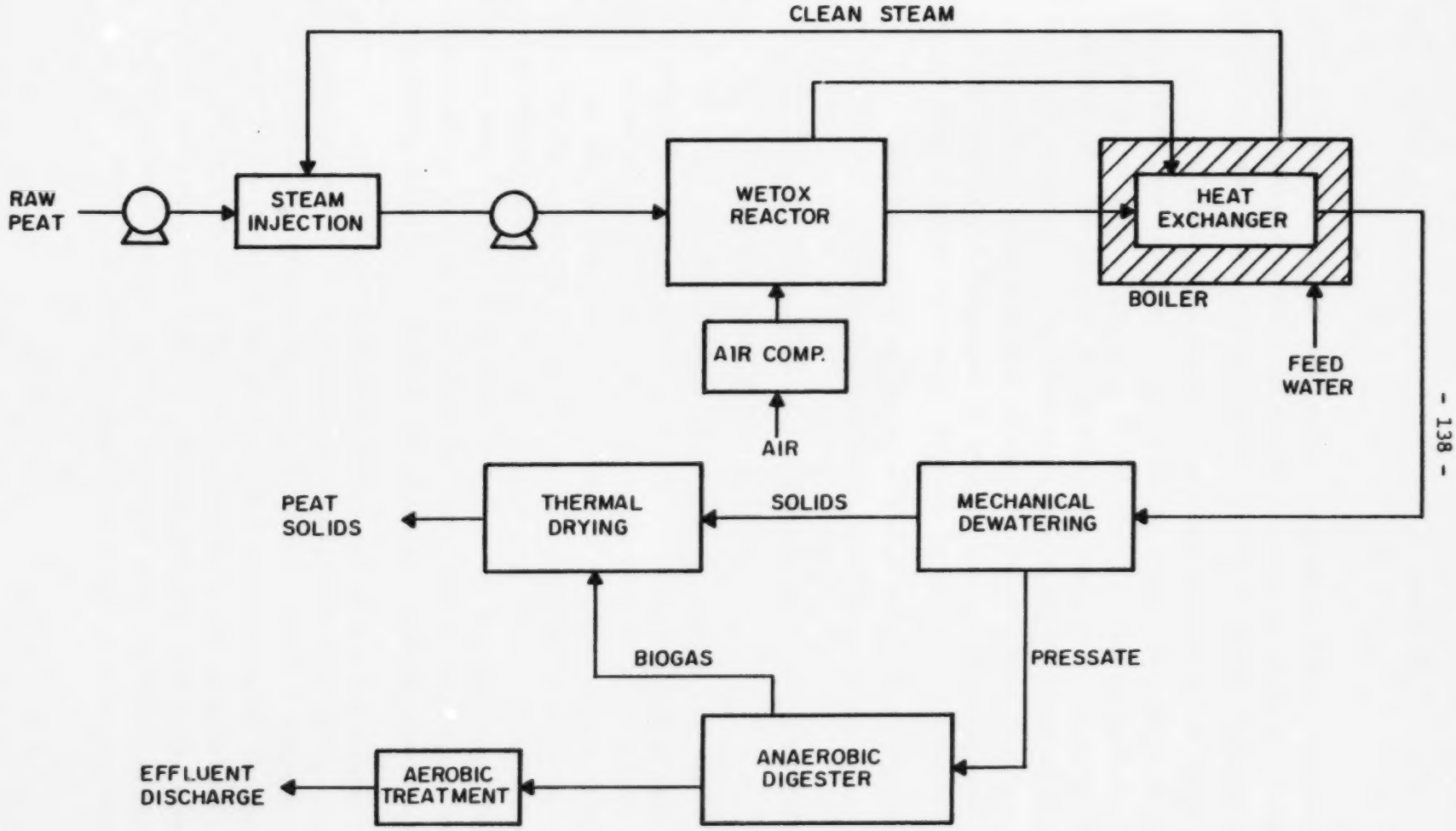

FIGURE 7.3 CASE 3. PARTIAL WET OXIDATION / DEWATERING OF PEAT.

press and thermal drier were obtained from Monenco (1981). Sufficient methane is produced to lower the moisture content to about 33%. The liquid effluent is polished aerobically before discharge to the environment.

The scale of the plant is 50 tonnes per hour of wet mined peat with solids concentrations evaluated in the range from 3.6% to 10.7%, producing peat fuel in the range of 1.1 to 3.3 dry tonnes per hour respectively. The solids concentration in the feed is one of the most important parameters in the plant design, exerting a strong influence on product cost. Unlike the case of total oxidation, there is only a limited range of feasible reaction temperatures and residence times that can be used to ensure that solids recovery is maximized.

More information on the plant design assumptions is contained in the description of the computer model, Sections 7.4.1 and 7.4.3.

7.4 Computer Model for Process Simulation and Economic Analysis

7.4.1 General Description

Two computer programs were prepared in order to facilitate the analysis of wet oxidation processes proposed in Cases 1 to 3. Given the appropriate kinetic data, the programs allow the calculation of yields and the economic evaluation of the processes under a variety of operating conditions. The program calculates the impact on economic parameters (operating and capital costs, energy costs, thermal efficiency and net power output) of such input variables as feed peat cost, feed concentration, process temperature and Wetox reactor temperature, the interactions being based on experimentally determined reaction kinetics.

The programs, designated WETXT 2 and WETX 4, are written in Fortran Version 4. With the appropriate password, they can be operated from a portable terminal over a telephone line. WETXT 2 models a process for the total wet oxidation of peat including anaerobic digestion of the liquid effluent. If desired, electricity can be generated from the hot water and steam (Case 2), otherwise the model calculates a selling price for thermal energy in $/GJ, based on a sink temperature of 32°C (Case 1). WETXT 2 contains a total of 431 lines, of which approximately

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100 are executable statements. WETX 4, used to model Case 3, is essentially the same as WETXT 2 with a number of minor modifications and additions. These are described in detail in Section 7.4.3.

The program contains a number of user-selected options. These options are used to test various process parameters and also select other unit operations in addition to wet oxidation such as anaerobic digestion and electrical generation.

The model is operated in a batch mode. The input data are read in, all the calculations performed and the results are transferred in tabular form to an output file which can then be printed out. Refer to Section 7.4.4.3.

7.4.2 Input Data

To operate the program, a number of data values must be supplied by the user. These values are contained at the end of the executable statements; there is no separate input data file. For WETXT 2, a total of 56 values is required, including six option decisions. The data are conveniently divided into sections based on the unit operation to which they are applied. The program, WETX 4, has two variables in addition to those of WETXT 2. These variables relate to solids recovery and are contained immediately preceding the options. The following is a list of the variables and associated data values used in the process simulations.

7.4.2.1 Wet Oxidation

Variable Name	Definition	Value of Parameter, e.g.
K101	Fast regime 1st order kinetic constant (automatically calculated based on reaction temperature if Arrhenius data available; otherwise K1 must be entered)	0 min^{-1}
K102	Slow regime 1st order kinetic constant	0.01 min^{-1}
KA	Arrhenius constant	4.111×10^{3}
KB	Arrhenius exponent	-1.04×10^{4}

Variable Name	Definition	Value of Parameter, e.g.
T10	Reaction temperature, initial value	232.2°C
RT10	Residence time, initial value	5.0 minutes
CODIN	Influent COD concentration, initial value	50 g/L
PL10	Waste treatment cost	254 $/tonne COD
EXSA	Excess air fraction	0.1
TIN1	Influent temperature	10°C
OVP	Reactor over-pressure fraction	0.5
FR10	Influent flow rate	50 tonnes/hr
MF	Material factor (for SS 316)	1.0
L10	Labour factor	19 man-hr/tonne
NSTEP	Number of unit operations	1.0
UHEX1	Overall heat transfer coefficient	0.204 MJ/hr-m^2-°C
HR	Hourly pay rate	10 $/hr
ELEC	Purchased electrical cost	0.05 $/kWh
*DRT	Step change in residence time	7.5 minutes
*DCOD	Step change in COD concentration	50 g/L
*DTEM	Step change in reaction temperature	19.4°C
*DRM	Step change in feed costs	0.8 $/tonne
BP	Balance of plant factor	3.0
IR	Interest rate fraction	0.18
LIFE	Plant operating life	20 years
*ITEMP	Number of temperature increments	3
*ICOD	Number of COD increments	3
*IRT	Number of residence time increments	5
*IRM	Number of feed cost increments	7

Please note that the variables marked with an asterisk (*) are used to increment key variables in a stepwise fashion, thereby generating an array of cost figures which, in turn, are used to determine the sensitivity of the process economics to these key variables.

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7.4.2.2 Anaerobic Digestion

Variable Name	Definition	Value of Parameter, e.g.
K1	Thermal conductivity of digester walls	2.74×10^{-3} MJ/hr-m-°C
K2	Thermal conductivity of digester roof	1.37×10^{-4} MJ/hr-m-°C
L9	Labour factor	19 man-hr/tonne
VN9	Value for nutrients	220 $/tonne
B9A	Pump cost coefficient	5.55×10^{-5} M$/m^3-hr
B9B	Packing cost coefficient	1.0×10^{-4} M$/m^3
B9C	Digester cost coefficient	4.75×10^{-3} M$/m^3
WALL	Digester wall thickness	0.5 metres
ROOF	Digester roof thickness	0.15 metres
PL9	Waste treatment cost	254 $/tonne COD
T9	Digester influent temperature	30°C
SSA	Surface area/volume ratio	75 m^2/m^3
DEAD	Dead space fraction	0.10
LFAC	COD loading rate	12 kg COD/m^3-d
TREAT	Treatability compared to bean blanching waste	0.8
RECYC	Recycle ratio	2.0
H2DR	Height to diameter ratio	1.0
TAMB	Ambient temperature	18°C
NR9	Nutrient requirements	0.2438 tonnes/tonne COD

Please note that the digester cost coefficient is multiplied by the digester volume raised to the exponent 0.6 to account for economies of scale. In addition, the installed digester cost has been adjusted downward from $\$200/m^3$ at 1000 m^3 to lessen the impact of the balance of plant factor in the final costing. This was considered necessary since no buildings would be required to house the digesters.

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7.4.2.3 Solids Recovery

Variable Name	Definition	Value of Parameter, e.g.
SOLU	Effluent soluble COD as a fraction of total starting COD	0.135
SREC	Final fraction of initial solids that are recovered	0.616

These two variables apply only to the program, WETX 4, for the calculation of partial oxidation and dewatering costs.

7.4.2.4 User Options

The following options are available to the user. To select a particular option, the user sets the variable or 'flag' to equal one. If the option is not desired, then the flag must be set to zero.

Flag	Effects
IFLTM	Increments the Wetox reaction temperature by the value of DTEM during each pass through the DO loop.
IFLCD	Increments the influent COD concentration by the value of DCOD during each pass through the DO loop.
IFLRT	Increments the residence time by the value of DRT during each pass through the DO loop.
IFLRM	Increments the feed cost by the value of DRM during each pass through the DO loop.
IFLAD	Selects anaerobic digestion for the treatment of the effluent from wet oxidation.
IFLEG	Selects electrical generation utilizing the hot water and steam from wet oxidation and methane from anaerobic digestion if selected.

Although the flag, IFLEG, is included in WETX 4 (partial oxidation, Case 3), it should always be set equal to zero to ensure that erroneous results are not produced. The electrical generation section is only applicable to total oxidation reactions.

7.4.3 Uncertainties

The major advantage to computer models is the large number of possible situations that can be evaluated very quickly and economically. Therefore, if uncertainties exist in key process variables,

a wide range of values can be tried and the results compared. This approach has been taken with four important parameters: feed cost of the wet mined peat, reaction temperature, residence time and raw peat COD or solids concentration. The effects of these parameters on the overall economics is discussed in Section 8. There are, however, a number of other variables for which little data are available and, although they are not considered as important, they could still have significant impact. These variables are:

(i) MF - materials factor. Preliminary indications are that peat is a non-corrosive material and SS 316 is more than adequate to use for equipment fabrication. Some savings would be realized if SS 304 could be used.

(ii) UHEX1 - heat transfer coefficient. Heat exchanger costs are a significant portion of the total plant cost. Conservative transfer coefficients have been used. More data are required on variations in fouling as a function of solids concentration and temperature. Alternatively, the (so far proprietary) novel JP-Energy heat exchanger performance and cost parameters may be included in the program at a later date.

(iii) TREAT - wet oxidation effluent treatability. Although preliminary results indicate no toxicity problems, further testing is needed to determine maximum COD loading to an anaerobic digester. Digestion of the effluent appears to be critical to the overall process economics.

(iv) Kinetic Parameters - The kinetics of the wet oxidation and wet carbonization reactions and their dependence on reaction temperature also influence the overall economics. It has been shown in the experimental section of this work that the nature of the peat does have a bearing on the reaction kinetics. Two consecutive first order reactions have been assumed to model the wet oxidation of peat. Although this model gives adequate predictions of COD conversion for the conditions examined, further research

will no doubt increase the sophistication of the model. The economic model used the kinetic parameters determined for Northern Ontario peat as a typical example. For other peats, especially if their degree of decomposition and botanical origin is different from the peat used as an example, the kinetics need to be determined experimentally and fed into the program.

An additional note of caution must be sounded here with respect to the use of batch kinetic data for the prediction of continuous flow process performance. The performance of the continuous flow pilot plant correlated well with batch data up to 20 minutes residence time at 240°C reactor temperature in the pilot plant, achieving 65% COD conversion. Beyond this point, the physical limitations of the pilot plant became evident as the maximum operating temperature and oxygen transfer capacity were reached. Therefore, the extension of the economic analysis beyond 65% COD conversion and 240°C reactor temperature is somewhat speculative at this time, awaiting confirmation through more elaborate pilot plant testing.

7.4.4 Logic and Execution

7.4.4.1 Total Oxidation, WETXT 2 Program

Both programs follow an essentially linear logic with a number of 'nested' DO loops performing iterative calculations. The program listing is given in Appendix D. The progression of the calculations is as follows:

(1) Read in data
(2) Start wet oxidation temperature loop (T10) and calculate COD removal constant (K101) using Arrhenius' equation. If sufficient kinetic data are not available, K101 is obtained from the input data.
(3) Start influent COD loop (CODIN).
(4) Start wet oxidation residence time loop (RT10).
(5) Calculate COD removal obtained with wet oxidation operated at conditions specified with initial data.

(6) Calculate waste treatment cost of wet oxidation effluent if anaerobic digestion has not been selected (IFLAD = 0).

(7) Calculate wet oxidation air requirements.

(8) Calculate the steam pressure given the reaction temperature T10. The Frost-Kalkwarf-Thodos equation obtained from Reid, Prausnitz and Sherwood (1977) is used. This equation requires an iterative solution, solved here with a 6-pass DO loop.

(9) Calculate the heat of vapourization of the steam (HVAP) using the Watson relation obtained from Reid, Prausnitz and Sherwood (1977).

(10) Calculate the steam production (STMF) in tonnes per hour using the vapour pressure (VPP), reactor over-pressure fraction (OVP) and the airflow (AIRF).

(11) Calculate the enthalpy of the steam (HSTM) using the heat of vapourization (HVAP), the steam production and the reaction temperature.

(12) Calculate the liquid effluent flow and enthalpy (HLIQ).

(13) Calculate the reactor off-gas enthalpy (HGAS).

(14) Using the COD load (CODL) and the COD removal (CODR), calculate the heat of reaction. This assumes 6000 Btu/lb of COD or 13,923 MJ/tonne of COD.

(15) Calculate the preheat temperature required (TIN2) and the corresponding heat exchanger duty (HEX1) given the flow rate (FR10) and initial temperature (TIN1). Since preheating of the peat is accomplished with the condenser in the binary generating cycle, if electrical generation is selected, HEX1 equals 0.

(16) Calculate the net thermal output (HNET) subtracting the preheating required (HEX1), adding compressor heat rejection, and assuming a sink temperature of 32°C (190°F).

(17) Calculate the pumping power and capital cost. Cost correlation from Peters and Timmerhaus (1980) for diaphragm pumps.

(18) Calculate the air compressor power and capital cost depending on the pressure required. Above 5.15 MPa (750 psi), three stages are required. Capital cost data are taken from Peters and Timmerhaus (1980); compressor power assumes adiabatic compression with interstage cooling, Perry (1973). Heat rejected into the compressor cooling water is added to net thermal output.

(19) Calculate the wet oxidation reactor volume and capital cost. Maximum working volume for single reaction is assumed to be 16 m^3, fabricated from 316 stainless steel. Cost information was provided by Toronto Coppersmithing (1981).

(20) Calculate required heat exchanger area for preheating duty (HEX1) using heat transfer coefficient (UHEX) from data. Countercurrent, multi-pass tube-in-shell design is assumed.

(21) Determine heat exchanger cost using cost data obtained from Peters and Timmerhaus (1980).

(22) Calculate labour required and associated costs using general labour formula for chemical processing industries from Jelen (1970).

(23) Begin anaerobic digestion section by checking option flag, IFLGAD.

(24) Calculate the COD loading to the anaerobic digester, COD2, in tonnes/day.

(25) Design the anaerobic digester using operating conditions and configuration as specified by the input data.

(26) Calculate the efficiency of the anaerobic digester in removing COD, based on design criteria and actual loading rate and working temperature.

(27) Calculate the hydraulic residence time in the anaerobic digester.

(28) Determine the expected heat loss and associated temperature drop in the digester, given the operating conditions and design configuration.

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(29) Calculate the recycle pumping energy requirements and cost.

(30) Calculate the costs of aerobic treatment of the digester effluent, assuming a charge of PL9 equals $254/tonne of COD.

(31) Calculate the volume of methane produced, assuming 0.35 m^3 of methane per kg of COD removed.

(32) Determine the quantity of nutrients that must be added to the influent and the corresponding operating cost, based on VN9 equals $220/tonne of fertilizer.

(33) Calculate the labour required to operate the digester, using the correlation of Jelen (1970), and the associated costs.

(34) The total operating cost for digestion (TOC9) is determined by adding energy, chemicals, labour and waste treatment costs.

(35) Calculate the energy available from methane by using 39.8 MJ/m^3 of gas.

(36) Determine the capital costs for anaerobic digestion by calculating pump, packing and reactor costs. Cost data for packing and reactor were supplied by the National Research Council (1982).

(37) If anaerobic digestion was not selected (IFLAD = 0), set variables to zero.

(38) Determine the overall net thermal power output (PWR) by adding the total energy content of the methane produced, ERC9, with no losses, to the net output from wet oxidation HNET.

(39) Begin the electrical generation section by checking the user-selected flag, IFLEG. If IFLEG equals 0, no electrical generation was selected. Therefore, skip the calculations.

(40) Determine the efficiency of the turbine-generator section, based on amount of superheating available. From data by Hensler and Axtmann (1979), maximum efficiency is about 17.2% with an additional 24% of the steam energy supplied by superheating. Efficiency adjusted downwards in proportion to shortfall of methane. If no methane is available, then efficiency is 12.8%.

(41) The capital cost for electrical generation is calculated based on data provided by Schapiro and Hajela (1979) for a 10 MWe plant based on geothermal energy. It is assumed that economies of scale vary to the exponent 0.6.

(42) The labour costs were obtained from the Standard Handbook for Electrical Engineers (1968), estimated at $0.20 per kW-year in 1967. This was converted to $0.069 per MW-hr in 1982 using the labour cost index in Chemical Engineering. Unfortunately this is at a scale of 1000 MWe; therefore, Jelen's exponent scale factor of 0.76 was used to adjust the rate, resulting in labour costs of $22.80 per hour for a 10 MWe plant.

(43) If electrical generation was not selected (IFLEG = 0), then the appropriate variables are set to zero.

(44) The overall thermal efficiency of the process is calculated using one of two equations, depending on whether electrical generation has been selected. With no electrical generation, the thermal efficiency is defined as the total net thermal output (HTOT) divided by the thermal equivalent of the electrical energy consumed, plus the potential energy of the raw peat feed. The thermal equivalent of the electrical energy assumes an efficiency of conversion of 33%. With electrical generation, the thermal efficiency is defined as the net thermal output (HTOT) times the efficiency of generation (EEFF) minus the electrical requirements of the process, all divided by the potential energy of the raw peat feed.

(45) The installed capital cost of the plant is calculated by adding the individual equipment costs and multiplying by the balance of plant factor, BP. A value of 3.0 is used for BP, higher than the normal value of 2.5 because of the extra reliability required of a generating plant.

(46) Calculate the total operating costs (OCST) by adding each cost from each applicable unit operation. Costs quoted are in $ per hour.

(47) The capital investment cost is converted to a $ per hour basis by using a capital recovery equation from Riggs (1968). A plant life (LIFE) of 20 years is assumed with an interest rate (IR) of 18% per year.

(48) Start raw material (peat) cost loop (RM), and calculate feed cost on a feed rate of FR10 tonnes/hour.

(49) Calculate final energy production costs based on either net thermal output or electrical power output if electrical generation option is selected.

(50) Print out results in a summary table. Refer to Section 7.4.4.3 describing output format.

(51) If more than one raw material cost is to be tested (IFLRM equals 1), then increment cost by the amount of DRM and return to start of the raw material loop.

(52) If the appropriate option has been selected, increment the associated variable by the amount specified in the data and return to the beginning of the loop. Each combination of selected values is thus tested by changing one variable and performing all the applicable calculations again. This is accomplished for the four key variables: raw material cost, residence time, COD concentration and reaction temperature, by this system of four nested DO loops.

(53) Once the calculations have been completed over the specified range for each variable, the execution of the program is stopped.

7.4.4.2 Partial Oxidation, WETX 4 Program

The program WETX 4 is used to evaluate Case 3, partial wet oxidation followed by mechanical dewatering and thermal drying. The program listing is given in Appendix E. Although the majority of the program is identical to WETXT 2, a number of modifications and additions were required. They are as follows:

(1) The soluble COD concentration in the wet oxidation effluent is calculated as a function of the total COD of the feed using the value for SOLU from the input data.

(2) The amount of steam required for preheating the raw peat by injection is calculated using a 5-pass DO loop iteration. This is required since addition of steam to the peat changed the COD concentration and the associated heat balance for the process.

(3) The quantity of dry peat solids recovered in the overall process and the corresponding energy content is calculated using the solids recovery factor, SREC, from the input data.

(4) A series of calculations are performed to determine the final moisture content of the recovered peat solids. Based on the bench-scale results and data provided by Sulzer Brothers Inc., it is assumed that mechanical dewatering achieves 50% moisture content which is then further lowered by thermal drying through burning the methane in the rotary drier. The drier requires 3800 MJ per tonne of water removed.

(5) Production of the clean steam for preheating the raw peat and dewatering the recovered solids adds to the capital cost of the plant. Boiler costs were obtained from Peters and Timmerhaus (1980) while costs for the Sulzer belt press and Heil rotary drier are from Monenco and Ontario Research Foundation (1981).

(6) Additional energy in the form of electricity is calculated based on 7.5 kWh per tonne of feed for mechanical dewatering and 14.6 kWh per tonne of water removed by thermal drying.

(7) The additional labour is calculated using 1 man-hour per 10 tonnes of feed to the mechanical dewatering press plus 1 man-hour per 8.2 tonnes of water removed via thermal drying. Reference: Monenco and Ontario Research Foundation (1981).

In addition to the above changes in WETX 4, the output format is modified to provide some additional information in addition to that in WETXT 2. This is described in Section 7.4.4.3.

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7.4.4.3 Output Format

The key process variables and important cost information are printed out in a summary table of results. Refer to Appendices F to H which contain the output from both WETXT 2 and WETX 4 over a wide range of operating conditions.

The output from WETXT 2 is divided into three main groups of columns plus a final column which lists the overall cost for energy production in either $/GJ or $/kWh if electricity has been generated. The first four columns indicate the specific values of the four key process variables used in the calculations: raw peat cost in $/wet tonne, the influent COD concentration in g/L, the wet oxidation residence time in minutes and the reaction temperature in degrees Celsius. The next three columns contain calculated costs: total operating cost in $/hour, installed Wetox reactor cost in 10^6 $ and the total capital cost of the plant (including balance of plant factor) in 10^6 $. The final group of three columns indicates process performance under the headings of: COD removal efficiency in the Wetox reactor as a percent, the overall net thermal efficiency of the process in percent and the net power output in megawatts.

The program, WETX 4, models a somewhat different process. Therefore, the output has been modified to provide different information. As in WETXT 2, the first four columns contain the important input data values: raw peat cost, COD concentration, residence time and reaction temperature. The next three columns contain the calculated quantities of: steam required for preheating the raw peat in units of tonnes per hour, the net heat available from the Wetox effluent in GJ/hour and the methane gas production from anaerobic digestion of the soluble COD also in units of GJ/hour. The final group of four columns lists the rate of production of dried peat solids in dry tonnes/hour, the moisture content of the final product in percent by weight, the capital cost of the plant in 10^6 $ and, finally, the production cost of the dried peat in $/dry tonne. In the last column, the dried peat cost is converted to an energy production cost in $/GJ.

8. TASK 6 - ECONOMIC ASSESSMENT

8.1 General

As it was described in Section 7 , three plant configurations were evaluated through process and economic modelling:

Case 1: "total" wet oxidation + anaerobic digestion, producing thermal energy.

Case 2: "total" wet oxidation + anaerobic digestion, producing electrical energy.

Case 3: partial wet oxidation + dewatering + drying, producing solid peat fuel.

All of the above configurations include final wastewater treatment by the aerobic activated sludge process.

The design programs incorporate experimental data obtained in the course of partial and total wet oxidation of Northern Ontario peat. The aerobic and anaerobic treatability of the effluents having been established experimentally, we have used the design and cost data of Van den Berg (1982) for the estimates of the anaerobic treatment system. The heat recovery system for electrical generation, its efficiency and cost parameters were based on the work of Schapiro and Hajela (1979), who published a design estimate for a 10 MWe geothermal energy recovery system for comparable thermal conditions. The programs were described in Section 7.4.

Up to 58 kinetic and cost parameters were initially fed into the design programs. These values are listed in Section 7.4.2.

The major advantage to computer models is the large number of possible situations that can be evaluated quickly and economically. Therefore, if uncertainties exist in key process variables, or optimum conditions are sought, a wide range of values can be tried and trends in the results may be discovered and evaluated. This approach has been taken with four important parameters:

- cost of wet mined peat feed
- feed peat solids (or COD) concentration

- Wetox reactor temperature
- Wetox reactor residence time

The effects of these variables on the overall process economics are discussed in this section.

As shown in Section 3, the cost or solids concentration of wet mined peat are not known with certainty at this time. The scale of operations evaluated and the mining and transportation methods proposed influence both the cost and the concentration of the mined peat slurry (Table 8.1). Therefore, it was decided to separate the feed cost and concentration parameters and generate sufficient cost data to estimate for conditions as they become known as a result of developments in peat wet mining technology.

The concentration of the peat feed is expressed in grams/litre COD, as determined by the chromic acid method (Section 4.2.3). The COD equivalent of peat solids varies between 1.2 and 1.45 grams COD per gram of volatile solids. It will have to be determined experimentally for the given peat sample. The thermal equivalent of COD is generally 13.9 GJ/kg COD (6,000 Btu/lb COD). (Zimmermann, 1958).

The temperature and residence time in the Wetox reactor has a strong effect on process economics in the total oxidation cases. Generating cost data with varying reactor conditions enabled us to determine optima with respect to capital and product cost. For the partial oxidation case, only one set of process conditions were found to be practical.

8.2 Total Oxidation

8.2.1 General

Two process configurations based on total oxidation of peat slurries in the wet oxidation reactor were evaluated. The term "total oxidation" must be used with some caution: experimental work showed that the extent of oxidation in the Wetox reactor in the presence of excess oxygen varies from 45 to 80% of oxidizable material fed, depending on reactor temperature and residence time and the nature of the peat.

TABLE 8.1 - Summary of Wet Mined Peat Costs

Source	$/dry tonne	Solids Conc. %	$/wet tonne*	Operating Scale**	Avg Delivery Distance, km
G. B. Morris (1982)	5.0	8	0.40	670 K	15
Monenco Ltd. (1981)	32.0	15	4.80	50 K - 200 K	15
Dravo Corp. (1982)	25.30	1	0.253	8520 K	16
	15.40	2	0.308	8520 K	16
	18.70	3	0.561	8520 K	16

*At given solids concentration
**Dry tonnes/year

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The unoxidized portion of the COD is almost completely solubilized and anaerobic digestion allows further energy recovery in the form of thermal or electrical energy obtained from the burning of the digester gas.

The two case studies elaborated below reflect forms of energy produced: thermal and electrical. For each case study, the effect of the many possible combinations of feed and reactor conditions were calculated. These effects were reflected in the thermal efficiency of the system, the amount of net delivered power, the capital cost and the cost of the delivered energy.

The evaluation was carried out in the following manner:

The concentration of the delivered peat slurry depends on yet to be developed wet mining technology. For a series of feed concentrations, the best reactor conditions were found, optimized to yield minimum delivered energy cost. The upper practical limit of macerated peat slurry concentration appears to be 10% suspended solids, corresponding to about 15% COD concentration. Thicker slurries do not appear to be pumpable in our experience. The lower limit of feed concentration was taken as 5% COD ($\sim$ 3.6% solids). Process economics deteriorate rapidly with increasing dilution.

For each feed concentration, at the optimum reactor conditions, the energy cost was plotted against a range of feed cost values. The energy cost varied linearly with feed cost, its sensitivity to feed cost being dependent on feed concentration.

Since the plant design estimating programs were based on a constant wet peat feed rate (50 wet tonnes/hour), the energy output and capital cost varied with the feed concentration, thermal efficiency and reactor conditions. In order to facilitate the comparison of capital costs for various conditions, a parameter was calculated by dividing the capital cost by the capacity of the plant to arrive at a "capital cost efficiency" in dollars invested per kW capacity constructed.

The major items of process equipment, viz. the Wetox and digestion reactors, have upper limits on their size (16 m^3 and 1000 m^3 respectively). Hence the plant is, by necessity, of modular construction

and will show little sensitivity to economies of scale. Therefore, at this level of estimating accuracy, the capital cost per unit of capacity parameter may be used to extrapolate plant costs to larger sizes.

With varying portions of the energy cost being attributed to operating charges, the minimum energy cost did not always coincide with minimum capital investment. It is evident that the choice of optimum conditions is sensitive to the prevailing interest rates (18% per annum was used here), but this variation was not evaluated at this time.

The overall thermal efficiency of each plant is determined by the thermal efficiency and degree of conversion in each chemical reactor and by the thermal conditions in the turbine-generator set, as described in Section 7.4.4.1. The overall thermal efficiencies were plotted for each case study for selected conditions.

Computer printouts of the economic evaluation of Cases 1 and 2 are reproduced in Appendices F and G.

The cost of energy produced is highly dependent on feed cost, and somewhat less so on feed concentration. The cost of feedstock is uncertain at the present time, although the $4.80/wet tonne figure is based on actual production experience. This mining operation is also the one delivering peat at the highest solids content, 15%. The sensitivity of costs to peat solids concentration suggests that, if the eventually selected mining method delivers a dilute slurry, it would be worth while to concentrate it to 10% solids. This is the maximum solids concentration which can be pumped over short distances, e.g. within the plant. Effective fuel peat slurry concentrating technology has not yet been developed.

The cost of energy production by this method is still higher than that of a cheap energy source such as natural gas. However, for remote locations, it may eventually become applicable, provided that energy costs rise and additional process developments are achieved. This development would concentrate on the optimization of the anaerobic digestion process, since this section is already more efficient than the

thermal section under the existing conditions. There is hope for this approach, since the laboratory digestion results showed that the organic acids produced through wet oxidation are directly usable to the microflora, and produce a better quality biogas (75% CH_4) than combined acidophilic-methanogenic fermentations (60% CH_4). Furthermore, the gaseous fuel produced by this route would be of greater general utility than the relatively low-temperature heat recovered alternatively.

8.2.2 Case 1

As shown in Figure 7.1, the flowsheet consists of wet oxidation of the raw peat slurry, anaerobic digestion of the Wetox effluents and aerobic treatment of the digester effluent. Thermal energy is recovered from the Wetox effluent streams and from the methane generated in the digester.

From Table 8.2, it is evident that the degree of COD conversion in the Wetox reactor is dependent on the reactor temperature and residence time. The efficiency of recovery of energy from the thermal section depends on feed concentration as well. The overall system thermal efficiency is defined as:

$$\frac{100\ [(\text{Heat recovered from Wetox}) + (\text{Heat recovered from Methane})]}{(\text{Heat content of Feed}) + (\text{Electrical energy supplied} \times 3)}$$

= Overall thermal efficiency, %.

Feed reference temperature is 10°C, heat recovery sink reference temperature is 32°C and the energy recoverable from biogas is taken as 39.8 GJ/m^3.

Overall thermal efficiency for the system is shown in Figure 8.1 and in the last column of Table 8.2. Since the thermal efficiency of energy conversion is generally higher in the digester than in the thermal section, the overall efficiency tends to decrease with increasing conversion through wet oxidation. As the feed concentration increases, so does the efficiency, since less water needs to be heated up and moved about.

TABLE 8.2 - Case 1 : Summary of COD Conversion and Thermal Efficiencies

Feed Concentration g/L COD	Reactor Residence Time minutes	Reactor Temperature °C	COD Conversion in		Thermal Efficiency		
			Wetox %	Digester %	Wetox %	Digester %	Overall %
50	5	232.2	47.6	64.1	25.46	64.1	51.0
	35	232.2	61.2	64.1	33.42	64.0	51.2
100	5	232.2	47.6	64.1	30.69	64.1	56.4
	35	232.2	61.2	64.1	38.4	64.1	56.3
150	5	232.2	47.6	64.1	32.45	64.2	58.2
	35	232.2	61.2	64.1	40.1	64.2	58.0
50	35	251.6	71.3	64.1	38.37	63.9	50.9
100	35	251.6	71.3	64.1	43.26	64.1	55.9
150	35	251.6	71.3	64.1	44.91	64.1	57.6
50	35	271.0	79.5	64.1	40.6	63.8	48.9
100	35	271.0	79.5	64.1	45.29	64.0	53.3
150	35	271.0	79.5	64.1	46.9	64.1	55.4

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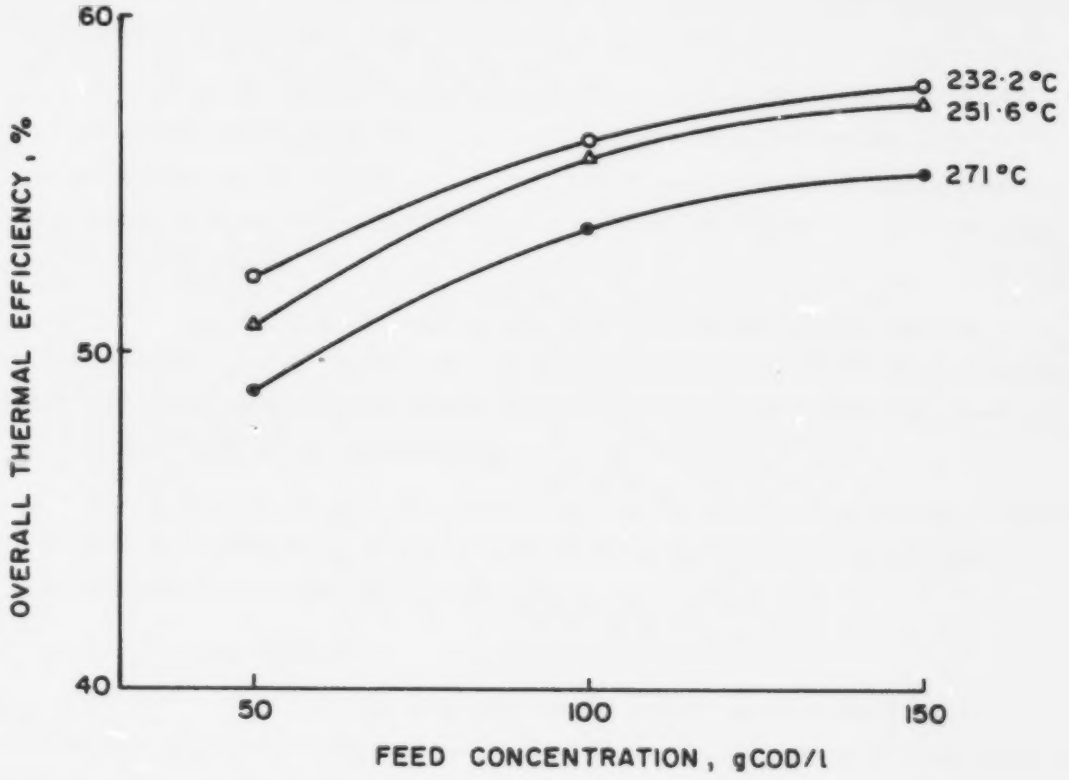

FIGURE 8·1 CASE I. OVERALL THERMAL EFFICIENCY AT 35 MINUTE RESIDENCE TIME.

The complex interactions of operating and capital costs with process conditions are clearly reflected in the cost of energy produced under various conditions. Setting aside the effect of peat feed cost for the time being, Figure 8.2 shows how the product energy cost changes with feed concentration and reactor conditions. Since the feed concentration may be determined by the wet mining technology, we have obtained from Figure 8.2 several sets of process conditions; some will yield the lowest energy costs for each feed concentration examined. These are 271°C reactor temperature at 35 minutes residence time for feed concentrations ranging from 50 to 150 g COD/litre.

The dependence of product energy cost on feed cost was found to be direct and linear, with the cost sensitivity increasing with decreasing feed concentration. The energy cost may be extrapolated to zero peat cost. The relationships are shown in Figure 8.3 for the optimum reactor conditions.

The effects of feed and reactor conditions on the capital investment are shown in Figure 8.4. Evidently, the lowest plant capital cost will not necessarily result in the lowest energy production cost under the conditions investigated.

Instead of giving a single value for the cost of energy produced in Case 1, a series of conditions were selected and capital and energy costs tabulated in Table 8.3.

8.2.3 Case 2

To convert the entire energy production from a combined peat wet oxidation and anaerobic digestion system to electricity, a binary steam generation cycle was proposed. The biogas generated in the digester was burned in a superheater. The superheated steam was converted to electricity in a turbine-generator set. The flowsheet is shown as Figure 7.2 and the design assumptions are given in Section 7.3.2.1.

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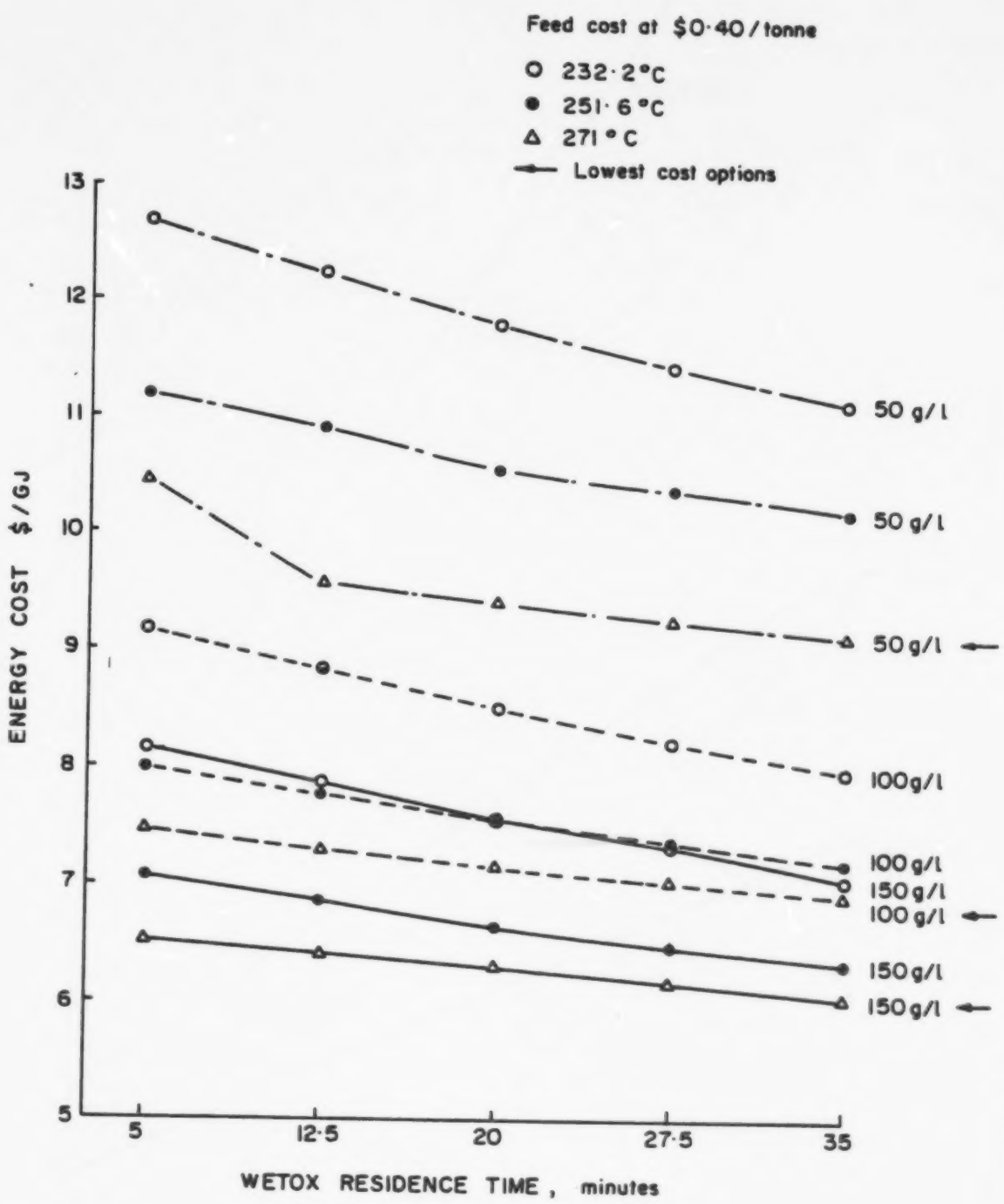

FIGURE 8·2 CASE I. ENERGY COST vs REACTOR CONDITIONS

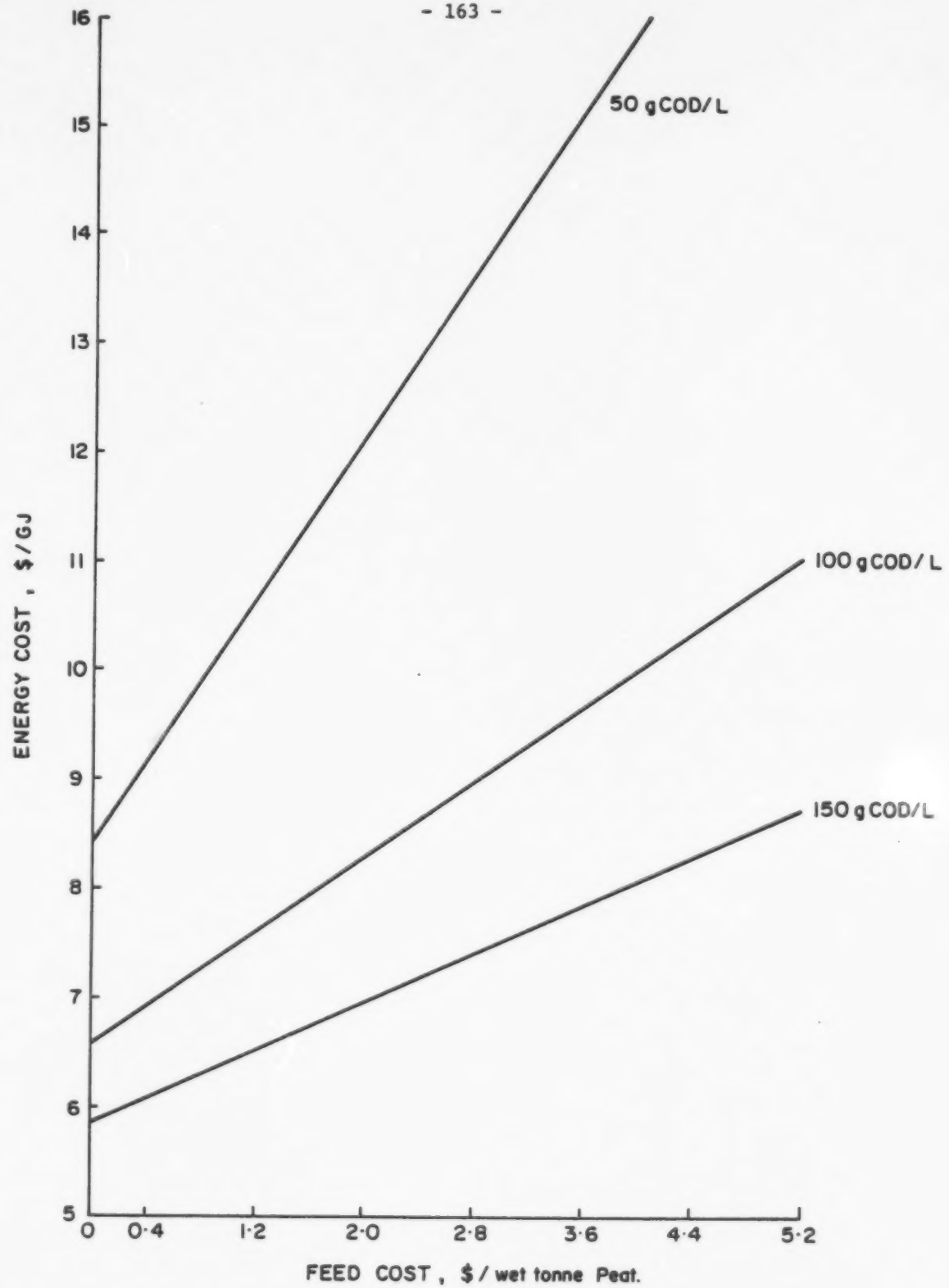

FIGURE 8·3 CASE I. ENERGY COST vs FEED COST AT BEST REACTOR CONDITIONS , 271 °C, 35 MINUTES

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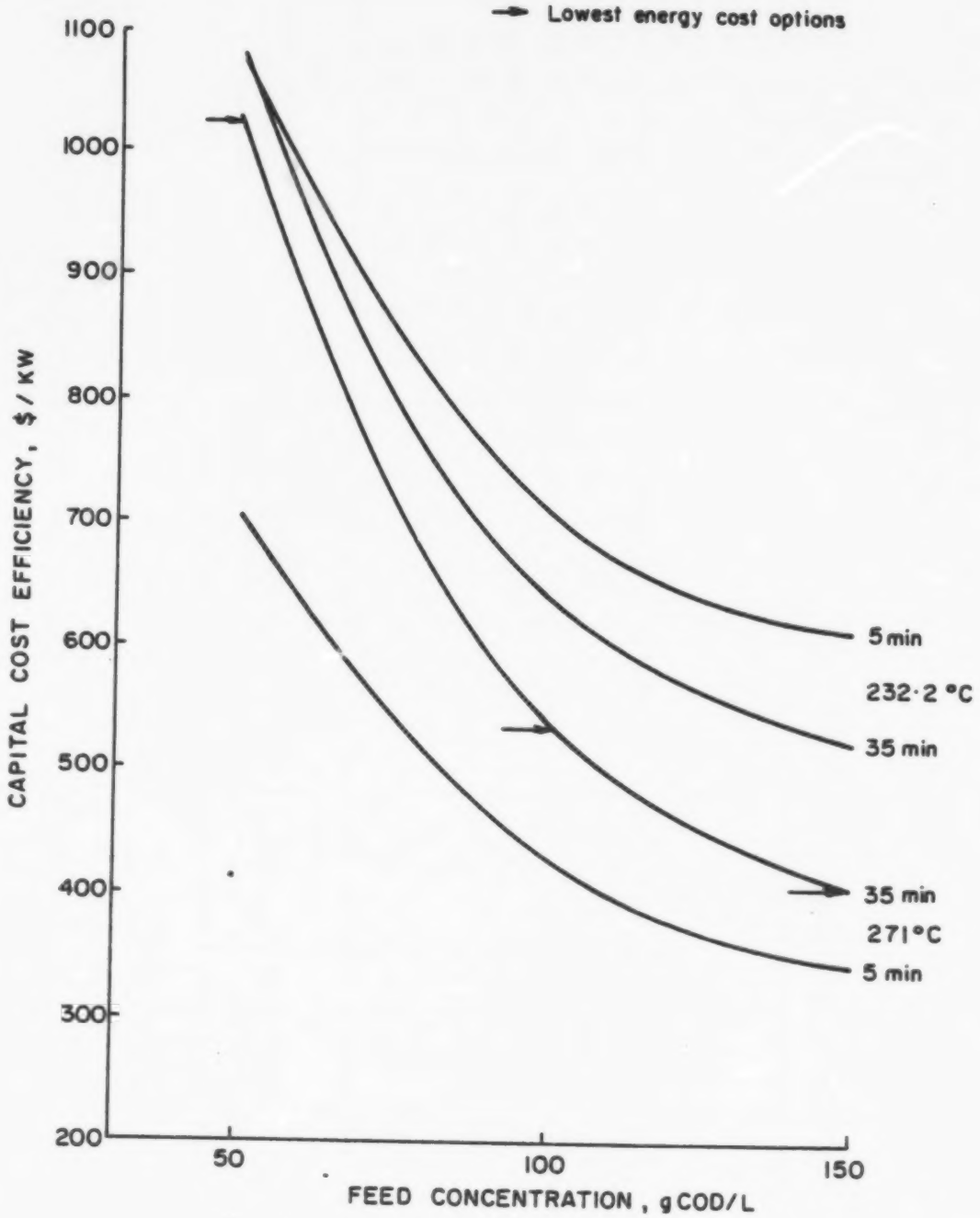

FIGURE 8·4 CASE I. CAPITAL COSTS

TABLE 8.3 - Case 1: Best Case Capital and Energy Costs

Feed Concentration g/L COD	Reactor Temperature °C	Wetox Residence Time minutes	Thermal Efficiency %	Energy Output MW	Capital Cost		Energy Cost	
					10^6 $	$/kW	@ $0.4/t* $/GJ	@ $4.30/t* $/GJ
50	271	5	48.9	8.1	5.7	704	10.48	18.96
50	271	35	48.9	8.4	8.6	1024	9.12	17.34
100	271	5	53.9	17.4	7.4	425	7.43	11.32
100	271	35	53.8	18.1	9.7	536	6.91	10.70
150	271	5	55.6	26.8	9.2	343	6.52	9.05
150	271	35	55.4	27.7	11.2	404	6.04	8.50

Basis: 50 wet tonnes/hour peat feed rate

*Feed Cost, $/wet tonne peat, delivered to plant

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The overall thermal efficiency is given by:

$$\frac{100\ [(T + G)E_g - (I_e)]}{F}\ \%$$

where, in consistent units:

T = thermal energy output of Wetox reactor
G = biogas energy equivalent, 39.7 MJ/m^3 CH_4
E_g = turbine-generator electrical conversion efficiency
I_e = internal electrical consumption (compressor, pumping)
F = feed energy equivalent, 13.92 MJ/kg COD

The electrical conversion efficiency, E_g, varies with the relative amounts of thermal and biogas energy available under the given operating conditions. According to Hensler and Axtmann (1979), maximum efficiency is about 17.2% when an additional 24% of the steam energy (T) is supplied by superheating (G). The efficiency is adjusted downwards in proportion to the shortfall of methane. If no methane is available, then the efficiency (E_g) is 12.8%.

The heat rejected by the turbine is recovered in the condenser to preheat the feed, and increases the value of T, and, therefore, raises the overall thermal efficiency.

The interactions of feed and process conditions are reflected in the overall thermal efficiency, and they are shown in Figure 8.5. Since the electricity used to drive the compressor is deducted from the production, and reactor pressure rapidly increases with reactor temperature, it is evident that, beyond 251.6°C and 5 minutes residence time, little or no net power will be available.

Because of the large electrical consumption of the compressors, best conditions for the range of feed concentrations are found at minimal Wetox treatment: 5 minutes @ 232.2°C, or 251.6°C. The unoxidized solubilized COD would be converted to biogas in the anaerobic digestion section, contributing to the energy yield and overall efficiency via the binary cycle superheater. The data generated for the economic analysis

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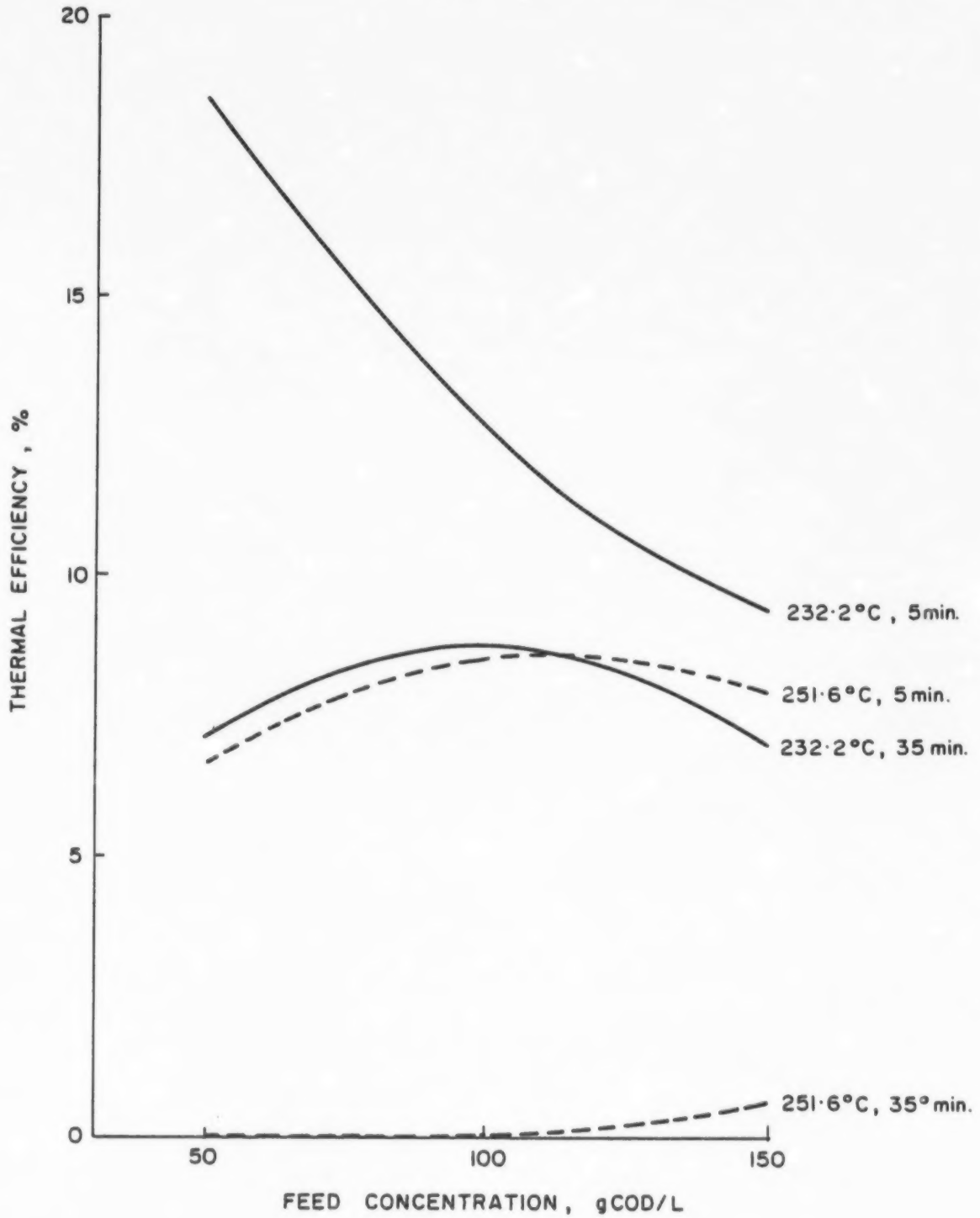

FIGURE 8·5 CASE 2. OVERALL THERMAL EFFICIENCY AT VARIOUS REACTOR CONDITIONS.

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of Case 2 is reproduced in Appendix F. The operating conditions yielding the lowest cost energy for three feed concentrations were identified from Appendix F and listed in Table 8.4.

The product energy cost again showed a linear dependency on feed cost, as in Case 1. In Figure 8.6 we plotted the variation of energy cost with feed cost at the optimum reactor conditions listed in Table 8.4 for each value of feed concentration. Capital costs were also calculated and expressed in $/kW capacity. The cost estimates were prepared for a plant operating factor of 100%.

The electrical energy production cost in this case is less sensitive to feed concentration than in Case 1, which suggests that capital costs and interest rates have a large influence in the selection of optimal operating parameters.

The cost of generated electricity falls between 0.140 to 0.258 $/kWh, which is not excessive for remote communities where petroleum fuel is trucked or flown in and power is generated on a small scale. For this reason, the technology described in this Case merits additional development effort to arrive at an optimized combination of the three conversion processes: Wetox, anaerobic digestion and electrical conversion.

8.3 Partial Oxidation, Case 3

The objective of the process proposed in this Case is the production of a solid peat fuel by a modified wet carbonization process. In order to avoid heat exchanger fouling problems which have plagued previous attempts at commercial wet carbonization, a portion ($\sim$ 10.7%) of the peat is burned in the Wetox/wet carbonization reactor. A portion of this heat keeps the reactor temperature at the operating level (204°C); another portion is recovered by raising steam in a boiler. This steam is injected into the feed slurry to raise its temperature sufficiently for overall heat balance to be maintained.

The treated peat is dewatered mechanically to 50% moisture content and further dried thermally. The energy for the thermal dryer

TABLE 8.4 - Case 2: Best Case Capital and Energy Costs

Feed Concentration g/L COD	Reactor Temperature °C	Wetox Residence Time minutes	Thermal Efficiency %	Energy Output MW	Capital Cost		Energy Cost	
					10^6 $	$/kW	@ $0.4/t* $/kWh	@ $4.80/t* $/kWh
50	232.2	5	18.6	1.9	7.3	3842	0.140	0.258
100	232.2	5	12.7	2.6	12.0	4615	0.149	0.234
150	251.6	5	7.9	2.6	13.7	5269	0.158	0.241

Basis: 50 wet tonnes/hour peat feed rate

*Feed cost, $/wet tonne peat, delivered to plant

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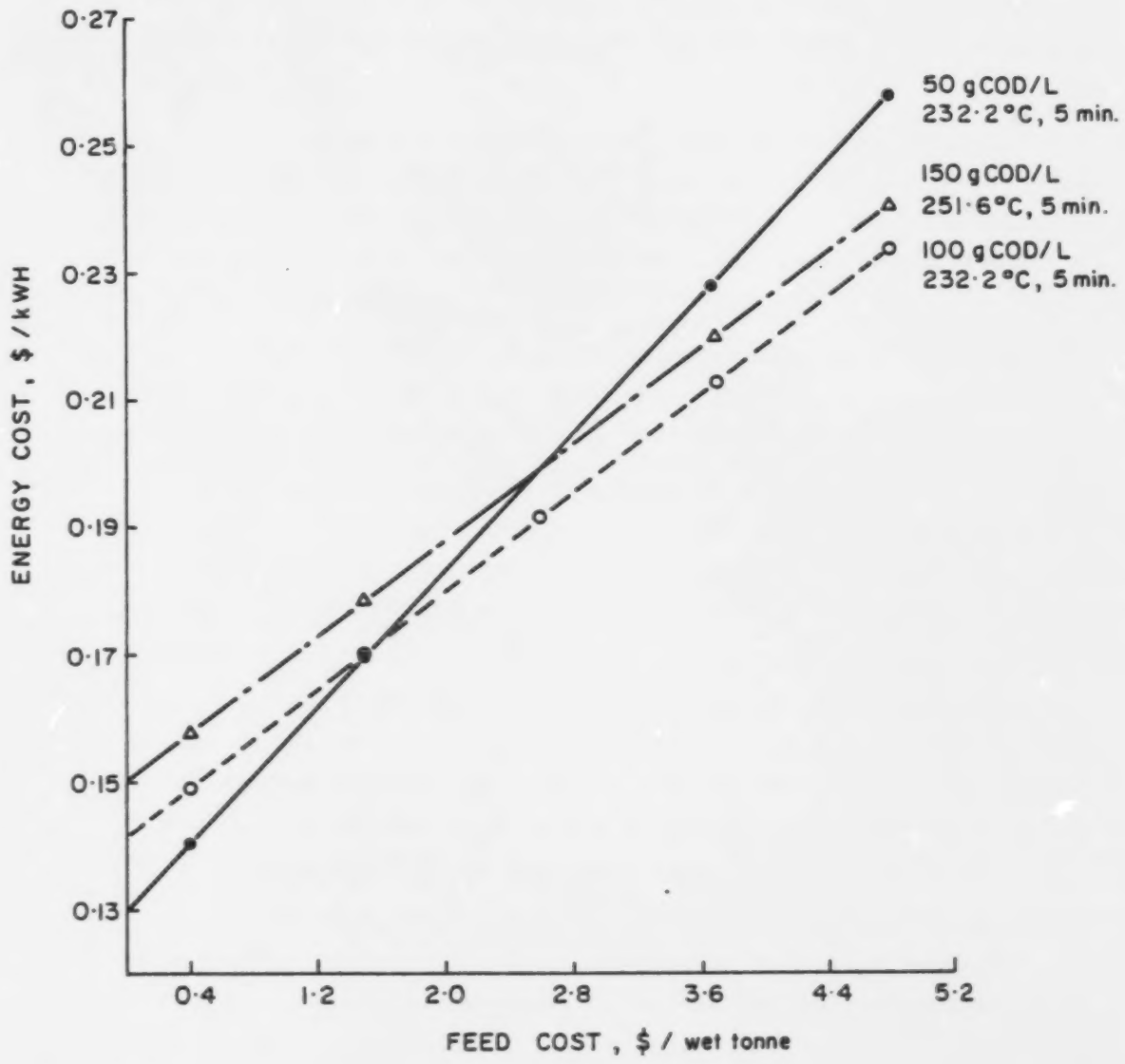

FIGURE 8·6 CASE 2. ENERGY COST vs FEED COST AT BEST REACTOR CONDITIONS.

is supplied by the biogas generated through the anaerobic digestion of the pressate liquor, which contains the solubilized portion of the feed solids, 13.5% of feed COD.

The flow schematic diagram is shown in Figure 7.3 A computer printout of the raw data generated for economic evaluation is reproduced in Appendix G.

On account of the uncertainty inherent in the feed cost and concentration figures, a series of product and capital cost values were generated for combinations of the feed conditions. Feed concentration ralues ranged from 50 to 150 g COD/litre; feed costs ranged from $0.40 to $4.80/wet tonne.

Only one reactor condition was evaluated, as it was found experimentally that 10 minutes treatment at 204°C gave satisfactory dewaterability. Lower temperatures were not as effective.

The design estimates were based on a feed rate of 50 wet tonnes of peat per hour, which meant that the plant production capacity was dependent on the feed concentration. Capital investment was calculated in the form of 10^6 $ investment per dry tonne/hour production capacity.

Pilot plant experiments showed that, if wet carbonization is accompanied by partial oxidation, the heating value of the recovered peat increases by 8% at 204°C reactor temperature. Calculated recoveries of feed solids on a moisture and ash-free basis ranged from 61.6 to 63.5%; feed energy content recoveries ranged from 66.5 to 68.6%.

The cost estimates were prepared for a plant operating factor of 80%. The product cost is rather insensitive to this parameter, as the application of 100% operating factor will decrease product costs by < 1%.

The final moisture content of the peat fuel was determined by the amount of heat available from the burning of the biogas by-product in the rotary drum dryer at the rate of 3.85 MJ/kg water evaporated (Heil Inc., personal communication). Without a source of external fuel,

moisture contents of ∿ 32 to 33% were attainable. This level of moisture content does render the peat suitable for gasification. Calculations showed that, if 17% of the peat can be solubilized, the additional biogas generated could reduce the product moisture content to 25%.

The variation of product cost with feed cost and concentration is shown in Figure 8.7. The cost of solid fuel produced increases linearly with increasing feed cost. A decrease in feed concentration increases product cost. The sensitivity of product cost to feed cost increases with decreasing feed concentration.

A summary of capital and product costs and product yields for the range of feed concentrations and extremes of feed costs is given in Table 8.5.

The concept of autothermal wet carbonization does appear to be technically feasible from our experiments. The high product costs obtained in the study ($85 and $159 per dry tonne at $0.40 and $4.80 per wet tonne of feed, respectively) result from the modest size of the plant (3.3 tonnes dry product/hour) evaluated here. By comparison, the JP-Energy process evaluation (Monenco, 1981) yielded dry product costs of $62.26 to $93.50 per tonne on 28.6 tonnes/hour production scale (mid-1982 estimates). The estimate carried out originally by JP-Energy OY in 1979 was based on quotations obtained on about 80% of the process equipment, whereas this study used a conservative (x 3.0) balance of plant factor on factored estimates of the major pieces of equipment (Sections 7.4.4.1 and 7.4.4.2).

Since the partial oxidation approach still is simpler than the elaborate heat exchange network used in the competing process, and the solids recovery rates are not greatly different (64.6% for JP-Energy versus ∿ 62% for partial oxidation), a more detailed process design on a larger scale would likely result in a more advantageous cost comparison for the partial oxidation route.

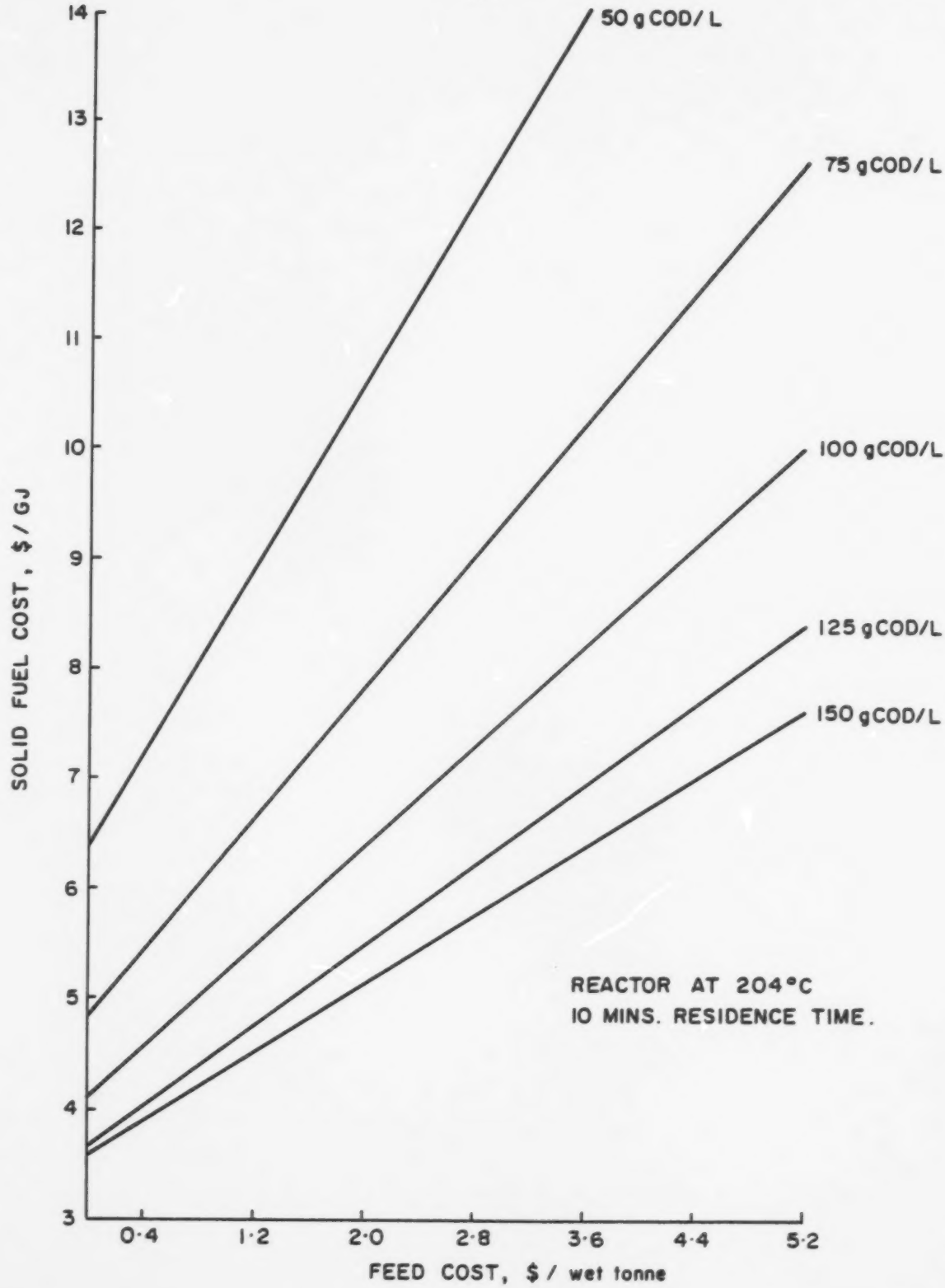

FIGURE 8·7 CASE 3. PARTIAL OXIDATION VARIATION OF PRODUCT COST WITH FEED COST AND CONCENTRATION.

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TABLE 8.5 - Case 3: Capital and Product Costs Summary

Feed Concentration g/L COD	Product Rate ** tonne/hr	Moisture Content* %	Product Yield % of Feed Energy	Capital Cost		Product Cost**			
						$/tonne		$/GJ	
				10^6 $	10^6 $-hr/tonne	@ $0.4/t	@ $4.8/t***	@ $0.4/t	@ $4.8/t
50	1.1	32.2	66.5	8.29	7.54	159	371	7.27	17.03
75	1.65	32.5	66.5	8.15	4.94	119	263	5.48	12.04
100	2.2	32.7	66.5	8.46	3.85	100	208	4.57	9.53
125	2.75	33.0	66.5	8.52	3.10	88	175	4.02	8.03
150	3.3	33.3	66.5	8.65	2.62	85	159	3.92	7.31

Basis: 50 wet tonnes/hour peat feed rate
* Product MC attainable with all of by-product methane used for thermal drying
** Dry basis
***Feed cost, $/wet tonne delivered to plant

Further economic model studies are required to determine the effects of oxidizing and solubilizing a larger portion of the peat to generate additional biogas to achieve a lower product moisture content. These conditions would have to be confirmed experimentally on the existing pilot plant.

Additional experimental work is required to explore the effects of autothermal wet carbonization on peats of lower degrees of humification.

9. ACHIEVEMENTS, FINDINGS AND RECOMMENDATIONS

9.1 Achievements of the Study

In the course of the study described in this report, the following tasks have been accomplished:

Task 1 From a review of information available to us, a range of costs for wet mined peat was determined.

Task 2 Total Oxidation

- Batch autoclave experiments determined the feasibility and kinetics of the total wet oxidation of peat slurries with their associated water contents. Three different peat samples of varied decomposition and botanical origin were examined.
- Continuous flow scaled-up experiments confirmed the simple kinetic model of the total wet combustion reaction for one wet-mined peat sample from Northern Ontario.

Task 3 Partial Oxidation

- Batch autoclave experiments established the feasibility and operating conditions for autothermal wet carbonization of peat slurries.
- Continuous flow pilot plant experiments confirmed the operating conditions and feasibility for autothermal wet carbonization of one wet-mined peat sample from Northern Ontario.

Task 4 Wastewater Treatment and Biogas Generation

- Continuous flow bench-scale experiments confirmed the treatability of wastewaters resulting from the wet oxidation of peat in anaerobic filters.
- Continuous flow bench-scale experiments established the treatability of anaerobic filter effluents in the activated sludge process.

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Task 5 Process Simulation

- Computer models were devised to evaluate mass, energy and economic balances for three process configurations:
  - thermal energy production through wet oxidation and anaerobic digestion of wet-mined peat (Case 1)
  - electrical energy production through wet oxidation and anaerobic digestion of wet-mined peat (Case 2)
  - solid fuel production through partial wet oxidation (autothermal wet carbonization) and anaerobic digestion of wet-mined peat (Case 3).

Task 6 Economic Assessment

- Employing the simulation programs, the yields, capital and product costs were determined for three design case studies listed under Task 5. The most economical operating parameters and costs were determined for a range of conditions.

9.2 Findings and Conclusions

Wet air oxidation is a process in which combustible material is oxidized by air or oxygen in the presence of liquid water. The process is operated continuously, with liquid and gas streams being introduced to the reactor simultaneously. Almost any combustible material which is retained in the liquid phase can be oxidized in the process. The combustion of the organic materials is achieved similarly in water at elevated temperature and pressure as by concentrating the material and incinerating the dry residue. The oxidation reaction generates heat which is recovered through heat exchange to preheat the incoming feed and generate steam for use elsewhere.

The patented Wetox process is carried out in a multi-compartmented horizontal reactor, provided with agitation and oxygen addition in each compartment. This arrangement results in substantially increased reaction rates over other wet air oxidation reactor designs. Since the wet oxidation process is carried out in dilute aqueous slurries, it appears to be suitable for the processing of wet-mined peat without prior dewatering.

Information concerning wet mining of peat was reviewed. Since wet mining is practised at only a few locations, cost and operating information is very scarce. Furthermore, most of the available information is based on feasibility study projections, rather than actual operating data. The mining and transportation costs are specific to the site, transportation distance, the solids content of the mined peat slurry and the scale of operations; therefore, it is difficult to generalize from the existing information.

The mined peat costs encountered in the literature ranged from $0.253 to $4.80 per wet tonne at solids concentrations of 1 to 15%, respectively. The figure most likely to reflect reality at the scale of processing evaluated in this study is $4.80/tonne, delivered at 15% solids content. The economic evaluation of the design case studies assumed a range of costs from $0.40 to $4.80 per wet tonne, and a solids concentration range from ∿ 3 to 11% (5 - 15% COD).

Three kinds of peat samples were treated in the initial total oxidation batch experiments:

- Sphagnum peat from the Trewartha bog in Northern Ontario, humification grade H9;
- Carex-Sphagnum peat from the Elma bog in Manitoba, humification grade H9;
- Wood-sedge peat from the Grand Falls area of Newfoundland, humification grade H5-6.

The pilot plant experiments of partial and total oxidation and the batch experiments of partial oxidation were carried out with Northern Ontario peat alone.

In batch reactions, the complete wet combustion of peat slurries follows the usual course of wet oxidation reactions: there is an initial rapid reaction, in the course of which 40-60% of the COD is oxidized within 5-12 minutes. The reaction that follows is about an order of magnitude slower, and an additional 5-15% of the initial COD is oxidized

during a total reaction time of 60 minutes. There is usually a well defined inflection point in the reaction curve, marking the completion of the initial reaction.

The two regimes of the reaction could be approximated by assuming two first-order differential equations:

$$\frac{d(COD)}{dt} = -K_1(COD) \qquad \text{to the inflection point,}$$

$$\frac{d(COD)}{dt} = -K_2(COD) \qquad \text{beyond the time of rate-change}$$

Drawing two intersecting straight lines on a plot of ln(COD) versus time, the two rate constants and the time of rate change may be determined for each total oxidation experiment.

The rate constant for the fast reaction (K_1) was temperature dependent, and this dependence followed the Arrhenius relationship:

$$K_1 = Ae^{-E/RT}$$

The second rate constant (K_2) showed no such correlation with temperature.

The total combustion of all three peat samples approximated the above model. Rate constants, rate change times, activation energies and frequency factors were determined for the three samples in the temperature range of 204 to 271°C, in the presence of excess oxygen. Using the appropriate constants for the sample and the reaction conditions, the extent of reaction could be predicted in the above temperature range with satisfactory accuracy. It is not intended to imply that the reaction is the sum of two simple first order reactions, but rather that this assumption is useful in characterizing the process and yields reasonably accurate predictions in the range of conditions surveyed.

The two highly humified sphagnum peats exhibited similar reaction kinetics in total oxidation. The medium-humified woody peat behaved differently: the first reaction was faster, but it terminated sooner with lesser extent of reaction. The activation energy suggested that oxygen transfer was the limiting process, probably at the surface of undecomposed solids.

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The kinetic approximation and parameters derived by batch reactions were verified through continuous flow experiments in a 4-compartment, stirred reactor of 35-litre capacity at residence times ranging from 12 to 29 minutes. The batch kinetics were transformed into the continuous mode by the method of Jones. At 232°C, COD reductions were predicted for 12, 20 and 29 minutes residence times to be 60, 67 and 70% respectively. The predictions correlated well with the experimental values of 62, 65 and 70% for Northern Ontario peat. Physical limitations of the equipment allowed only one temperature (232°C) to be investigated. A limitation to oxygen transfer in the reactor was also identified. The viscosity of the macerated peat slurry limits the maximum pumpable solids concentration to 10%. Without previous maceration, both the pumpability of the slurry and the speed of the initial reaction decrease substantially.

Catalytic effects of copper, nickel and cobalt ion additions were investigated in the batch reactor with the highly humified peat samples. At 400 mg/L Cu^{++} concentration at 232°C the value of K_1 increased about twofold and the extent of reaction increased about 25%. Nickel showed some positive catalytic effect at 400 mg/L concentration and 271°C. Cobalt was without effect.

To confirm catalytic effects at continuous flow, copper ion was used at 200 and 400 mg/L. The reaction rate increased noticeably but the extent of the reaction still plateaued at 67%. Therefore, it was concluded that the use of catalyst did not warrant the additional expense and process complexity.

To investigate the feasibility of autothermal wet carbonization by partial oxidation of the peat slurry and to obtain parameters to guide the pilot plant experimentation, batch autoclave experiments were undertaken, varying the temperature from 163 to 204°C, the oxygen dosage from 0 to 25% of TCOD and the residence time from 0 to 40 minutes. The conditions sought were those resulting in a mechanically dewaterable cake to < 50% moisture content and maximum heating value recovery through filtration and pressing at ∿ 3.3 MPa. The batch experiments identified the minimum temperature of 177°C and 10 minutes residence time to achieve the

desired results, with the expectation that 10 minutes at 204°C would result in a greater degree of oxidation and heat production and possibly better dewaterability.

The partial oxidation pilot plant experiments were carried out at 177 and 204°C and 10 minutes residence time on a Northern Ontario peat slurry of 6.1% solids concentration (9.6% COD). The product of the lower temperature reaction could be mechanically dewatered to not more than 35.2% solids content, which was deemed unsatisfactory. Treatment at 204°C yielded a pressed cake of 48.8% solids content, whose heating value increased by 8% over the raw peat to 21.8 MJ/kg. Solids recovery was 61.6%; 13.5% of the feed was present in the combined waste liquors as soluble COD. 10.7% of the feed was oxidized under these conditions. An additional 16.7% of feed COD was lost through unidentified reactions. The subsequent plant design estimate was based on these results, except that a 50% solids content pressed cake was assumed.

A variable portion of the feed peat solids is solubilized and appears in the wastewaters. The degree of solubilization ranges from 13.5% for partial oxidation to 20-60% of the feed COD for "total" oxidation. The soluble substances consist of simple organic acids (acetic, formic, etc.) and breakdown products of lignin oxidation. To recover chemical energy locked into these molecules, anaerobic digestion appears to be eminently suitable. Bench scale experiments with two horizontal, four-chambered packed bed digesters confirmed this expectation. Problems were encountered with pH control and subsequent ammonia toxicity in the experimental apparatus, and the available time (4 months) for acclimatizing the microflora was also too short. Therefore, maximum COD loading rates could not be determined at this time. In the one experiment where free ammonia concentration was within an acceptable range, COD removal efficiency of 75% was obtained.

The concentration of methane in the biogas was 70-75%, which is somewhat higher than that observed in other studies of the biogasification of peat (55-60%). The methane-rich nature of the evolved gases is a particular advantage of the wet oxidation pretreatment of peat: the

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fermentation of complex organics to volatile acids results in the evolution of CO_2, which is avoided in this case, since the acid production takes place in the Wetox reactor.

For the purposes of preliminary design, a treatability factor of 0.8 (compared to bean blanch wastewater) and a loading rate of 12 kg COD/m^3.day were assumed.

The BOD_5 content of the anaerobic digestion effluents were effectively reduced by aerobic treatment in an activated sludge system. At the F/M ratio of 0.13, over 98% BOD_5 removal was achieved, resulting in the effluent BOD_5 of 45 mg/L at 233 mg/L suspended solids. The wastewater treated in the bench scale aeration cells was not toxic to nitrifying bacteria. After a suitable acclimatization period, 99% of the feed ammonium nitrogen (315 mg/L) was converted to nitrate.

Through mathematical modelling of performance and cost parameters, three design case studies were undertaken:

Case 1: total wet oxidation + anaerobic digestion, producing thermal energy

Case 2: total wet oxidation + anaerobic digestion, producing electrical energy

Case wet oxidation + dewatering + drying, producing a solid peat fuel.

The design programs incorporate experimental data obtained in the course of partial and total wet oxidation of Northern Ontario peat. The estimation of anaerobic and aerobic treatments and the electrical conversion via a binary cycle and turbine-generator set were based on published studies.

Thermal efficiencies, capital and product costs were influenced strongly by some or all of the following major parameters. Their effects were evaluated by varying them in the ranges shown:

- cost of wet mined peat feed ($0.4 to $4.80 per wet tonne)
- feed peat solids (or COD) concentration (50 to 150 g COD/L)

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- Wetox reactor temperature (232.2 to 271°C)
- Wetox reactor residence time (5 to 35 minutes)

The design basis was 50 wet tonnes/hour feed rate. Since the processes will be by necessity of modular construction, the overall capital cost will show little sensitivity to economics of scale. The product costs included 18% interest on 100% of the investment, with a plant life of 20 years and no salvate value.

For Cases 1 and 2, optimum reactor conditions (based on minimum product cost) were established for three feed concentration values. The dependence of product cost on feedstock cost was established next, followed by the calculation of capital investment per kW capacity constructed, for each feed concentration, at the optimum reactor conditions. Cost parameters were tabulated in the report for each case, for a range of conditions.

In summary, the lowest energy costs for Case 1 are achieved at 150 g COD/L feed concentration at 271°C. The energy output of the plant at 50 wet tonnes/hour feed rate is 27.7 MW at a thermal efficiency of 55.4% with a heat sink reference temperature of 32°C (90°F). If the feed costs $0.40/wet tonne, the product energy costs $6.04/GJ; at $4.80/wet tonne feed cost, the energy is produced for $8.50/GJ. Total capital investment for this plant would be $11.2 x 10^6.

For Case 2, the lowest energy costs are obtained at 150 g COD/L feed concentration at 232.2°C reactor temperature and 5 minutes residence time. The electrical generating capacity of the plant at 50 wet tonnes/hour feed rate is 1.9 MWe at a thermal efficiency of 18.6%. If the feed costs $0.40/wet tonne, the product energy costs $0.140/kWh; at $4.80/wet tonne feed cost, the energy costs $0.258/kWh. Total capital investment for this plant would be $13.7 x 10^6. Higher feed concentrations resulted in generation costs which were not much different from these; however, thermal efficiency decreased and capital cost increased significantly.

For Case 3, only one reactor condition was evaluated, as it was found experimentally that 10 minute treatment at 204°C gave satisfactory dewaterability. The analysis of capital and product cost dependence showed that the process becomes increasingly economical with increasing feed concentration. Anaerobic digestion of the wastewaters and combustion of the resulting biogas produced a 35% moisture content fuel at about 66% feed energy recovery. Minimum product costs were $3.92 and $7.31 per GJ for $0.40 and $4.80/wet tonne feed cost respectively at 150 g COD/L feed concentration and 21.8 GJ/kg product heating value. An installation producing 3.3 tonnes/hour dry product is estimated to cost $8.65 x 10^6.

9.3 Recommendations for Further Development

(1) Considering the technical and economic merits of the three case studies evaluated, those dealing with electrical generation and solid fuel production warrant further development effort. A third option became evident towards the end of the study: optimizing the thermal and biological processes towards the production of biogas and adding gas cleaning facilities to produce substitute natural gas (SNG) from wet mined peat.

It is recommended that deciding on the direction of future development be the subject of a system study. Using the existing process models, the systems should be further optimized, projecting required performance parameters which would need to be realized in order to render the processes economically justifiable. Employing standard methods of R & D strategic planning, the probabilities and costs of achieving these results in practice would be estimated and the most cost effective route for development selected. This study would have to consider the broader context of fulfilling government and private sector objectives through the application of the developed process.

The necessary additional technical developments need to be addressed on two fronts:

(a) the anaerobic digestion process is to be optimized. This section is already more efficient than the thermal process under the existing

conditions. This approach is likely to be fruitful, since the laboratory digestion results showed that the organic acids produced through wet oxidation are directly usable to the microflora which thereby produce a better quality biogas (75% CH_4) than the combined acidophilic-methanogenic fermentations (60% CH_4). Furthermore, the novel digester configurations being developed at the National Research Council will likely show superior performance to the reactors which formed the basis of peat biogasification work at IGT and Dynatech.

(b) further refinement of the autothermal wet carbonization process design is recommended, in view of the process concept which is simpler than the competing design proposed by JP-Energy OY. Economic model studies are required to define the optimum degree of solubilizing the peat to achieve a lower product moisture content. These conditions would then be confirmed experimentally in the existing pilot plant. A more detailed process design on a larger scale would likely realize additional improvements of product cost.

Additional experimental work is required to explore the effects of autothermal wet carbonization on peats of lower degrees of humification.

In order to be able to realize the advantages of the wet processing of peat, these additional areas were identified which are in need of development.

(2) Considerable development work is required to establish the costs of wet mining of peat. Such a study would preferably be done specific to a site chosen for the subsequent demonstration of one of the wet oxidation processes. It is evident from the process studies described in this report that the concentration of the feed slurry strongly affects the economic performance, with higher feed concentrations being more advantageous. Therefore, the wet mining studies will need to specify and confirm the mined solids concentrations.

(3) Certain aspects of wet mined peat slurry pretreatment need development. It is known that raw peat slurries over 3% solids concentration cannot be pumped without expending excessive amounts of energy. This fact, plus the observation of improved reaction kinetics in wet oxidation necessitate grinding or macerating of the concentrated peat slurries before hydraulic transport. There is a need for selecting and investigating the performance of suitable equipment for this purpose, as well as the determination of energy losses in the pumping of macerated slurries.

(4) If the mining studies show that the practical peat slurry concentrations are likely to fall significantly below 10% solids, suitable methods for thickening the slurry need to be selected or developed and their costs and performance evaluated.

(5) All three wet oxidation process scenarios necessitate extensive heat exchanger installations for preheating the peat slurry prior to wet oxidation and for the recovery of energy from the effluent streams. Peat slurries are notoriously difficult to treat in conventional (indirect) heat exchangers, because of their viscosity and fouling characteristics. Although certain novel heat exchanger configurations have been tested (IGT, JP-Energy) and patented, (Myreen), nothing is published about the cost or operating characteristics of these units. Before further development of the wet oxidation of peat, additional information will have to be developed in this area.

REFERENCES

American Society for Testing and Materials (1980): "Annual Book of ASTM Standards", Part 31. ASTM, Philadelphia, Pa.

van Amstel, J. J. A. P. (1971): "The Oxidation of Sewage Sludge in the Liquid Water Phase at Elevated Temperatures and Pressures". PhD. Thesis, Technical University, Eidhoven, Netherlands.

Bettinger, J. A. (1982): "Peat Combustion and Enhancement by Wet Oxidation". Unpublished Report, Michigan Technological University.

Brett, R. (1968): "Carbohydrate Oxidation with Hydrogen Peroxide at Elevated Temperature and Pressure". PhD. Thesis, Illinois Inst. of Tech. University Microfilms Inc., Ann Arbor, Mich.

Buivid, M. G., Wise, D. L., Rader, A. M., McGarty, P. L., and Owen, W. F. (1980): "Feasibility of a Peat Biogasification Process", Resource Recovery and Conservation, 5: 117-138.

Cederquist, C. N., Bering, P. (1952): Acta Polytechnica No. 105. Chemistry inc. Metallurgy Series 3 (1): 5-34.

Cederquist, C. N. (1955): "Våt förbränning". Svensk Papperstidning 58: 154-164.

Chornet, E. (1980): "Feasibility Study of the Dewatering of Peat Using a High Velocity, Short Residence Time Reactor". Sandwell-Beak Research Group Report to the National Research Council of Canada; Project: R5058.

Chowdhury, A. (1974): "Catalytic Oxidation of Strong Waste-Waters". PhD. Thesis, University of Denver, Colo. University Microfilms, Ann Arbor, Mich.

Chynoweth, D. P., Srivastava, V. J., Henry, M. P., and Tarman, P. B. (1980): "Biothermal Gasification of Biomass". Presented at the Symposium on Energy from Biomass and Wastes IV, Lake Buena Vista, Florida.

Dettinger, T. P., Fontana, M. G. (1976): "Austenitic Stainless Steels and Titanium for Wet Air Oxidation of Sewage Sludge". Materials Performance, 15: 29-35.

Fuchsman, C. H. (1980): "Peat, Industrial Chemistry and Technology". Academic Press, New York, pp 12-18.

Gas Research Institute (1980): "Feedstock Characteristics and Preparation for Peat Gasification". Final Report for Phase 1. Contract Number 5014-310-0256.

Gooderham, P. (1981): Personal Communication, Toronto Coppersmithing International Ltd., Toronto, Ontario.

Hensler, J. M., Axtmann, R. C. (1979): "Cost Study of Superheating Geothermal Steam". Energy, Vol 4, 365-371.

Hudak, W., Dravo Corporation, Pittsburgh, Pa. (1982). Personal communication of unpublished results.

Institute of Gas Technology (IGT), (1981): "Experimental Program for the Development of Peat Gasification". Interim Report No. 9. U.S. Department of Energy Contract No. EX 76-C-01-2469.

Jelen, F. C. (1970): "Cost and Optimization Engineering", McGraw-Hill Book Co.

Jones, R. W. (1951): "Designing Continuous Reactors in Series from Batch Reaction Data". Chem. Eng. Progr. 47: 46-49.

Knechtel, J. R. (1978): "A More Economical Method for the Determination of Chemical Oxygen Demand". Water and Pollution Control, 116: 285-288.

Martinell, R, Hallberg, R., and Flygare, P. (1981): "Recovery of Organic Gases from Ground, Rock or Bottom Sediments in Lakes". Canadian Patent No. 1,098,062.

Mensinger, M. C. (1980): "Wet Carbonization of Peat: A State of the Art Review". Presented at 1980 IGT Conference, Arlington, Va.

Mohr, A. W. (1976): "Mechanical Dredges". Proc. Speciality Conference on Dredging and Its Environmental Effects, January 26-28, 1976.

Monenco Ltd. (1978): "The Mining of Peat - A Canadian Resource". Energy, Mines & Resources, Canada.

Monenco Ltd. (1981): "Evaluation of the Potential of Peat in Ontario". Occasional Paper No. 7, Ministry of Natural Resources, Ontario.

Morris, G. B. (1982): "Study of the Technology and Costs Associated with the Dredging and Overburden Removal Operations for the Recovery of Peat". National Research Council, Canada. Contract 01SX.31155-1-2643, by Kesmark Ltd., Toronto, Ontario.

Othmer, D. F. (1979): "Air + Water + Air = Fire". Mechanical Engineering, 101 (12): 30-37.

Othmer, D. F. (1980): "Peat Processing by Wet Oxidation". IGT Symposium on Peat as an Energy Alternative, Arlington, Va.

Perry, R. H., Chilton, C. H. (1973): "Chemical Engineers Handbook", 5th Edition, McGraw-Hill Book Co.

Peters, M. S., Timmerhaus, K. R. (1980): "Plant Design and Economics for Chemical Engineers", 3rd Edition, McGraw-Hill Book Co.

Reid, R. C., Prausnitz, J. M., Sherwood, T. K. (1977): "The Properties of Gases and Liquids", 3rd Edition, McGraw-Hill Book Co.

Riggs, J. L. (1968): "Economic Decision Models for Engineers and Managers". McGraw-Hill Inc.

ORI

Rohrer, J. W. (1980): "Wet Carbonized Peat-fuel and Feedstock". Presented at 1980 IGT Conference, Arlington, Va.

Ruoff, C. F., et al (1980): "Continued Development of a Peat Biogasification Process". Paper presented at 1980 IGT Conference, Arlington, Va.

Schapiro, A. R., Hajela, G. P. (1977): "Geothermal Power Cycle Analysis". 12th Intersociety Energy Conversion Engineering Conference Proceedings, 1977.

Standard Handbook for Electrical Engineers (1968), McGraw-Hill Inc.

Strehlenert, R. W. (1915): "Process of Utilizing the Organic as well as Inorganic Constituents of the Waste Liquor Produced by the Boiling of Sulfite Cellulose". U.S. Patent 1,149,420.

Van den Berg, B. (1982): Personal Communication, National Research Council, Ottawa, Ontario.

Vanasse, R., Coupal, B., and Boulos, M. I. (1979): "Hydraulic Transport of Peat Moss Suspensions". Can. J. Chem. Eng. 57: 238-241.

Water Pollution Control Federation (1980): "Standard Methods for the Examination of Water and Wastewater". 15th Edition, American Public Health Association, Washington, D.C.

Wise, D. L., Cooney, C. L., and Augenstein, D. C. (1978): "Biomethanation Anaerobic Fermentation of CO_2, H_2 and CO to Methane". Biotechnol. Bioeng. Vol 20, p 1153-1172.

Zimmerman, F. J. (1954): "Waste Disposal". U.S. Patent 2,665,249.

Zimmermann, F. J. (1958): "New Waste Disposal Process". Chemical Engineering, August 17, 1958, p 117-120.

APPENDIX A

Total Oxidation Raw Data

TOTAL OXIDATION OF PEAT - EXPERIMENTAL DATA

Peat Sample: Northern Ontario

Exp. Code	Reactor		Feed Concentration % COD	COD Reduction		Rate Change; minutes	K_1 min^{-1}	K_2 min^{-1}
	Temperature °C	Pressure MPa		t = 10 m %	t = 20 m %			
88	121	1.48	0.5	20.8	21.1	3.0	0.066	0.0029
89	121	1.48	0.5	21.0	22.0	3.0	0.068	0.0029
90	149	2.07	0.5	6.9	20.2	-	-	0.011
91	149	2.07	0.5	5.4	22.1	-	-	0.01
92	177	2.17	0.5	35.0	43.0	16.0	0.039	0.014
93	177	2.17	0.5	36.0	44.1	16.4	0.040	0.014
94	204	2.86	0.55	40.0	51.0	8.0	0.059	0.017
95	204	2.86	0.55	40.0	52.0	9.1	0.059	0.017
B	232	4.58	0.5	57.6	63.4	5.1	0.129	0.011
C	232	4.58	0.635	60.2	64.7	7.9	0.126	0.077
29	232	4.58	0.455	45.1	56.0	12.2	0.0603	0.0089
42	232	4.58	0.496	77.8	83.9	10.4	0.141	0.0094
SP2	232	4.58	0.555	62.2	71.2	10.4	0.101	0.021
SPR	232	4.58	0.555	71.2	80.0	10.2	0.123	0.015
52	232	4.58	0.609	73.7	83.3	6.2	0.181	0.015
52A	232	4.58	0.609	74.1	81.3	8.0	0.177	0.017
36	246	5.27	0.52	76.9	82.7	5.4	0.196	0.0147
43	246	5.27	0.496	77.8	84.9	10.5	0.140	0.0101
96	246	5.27	0.635	62.0	68.2	3.7	0.185	0.021
97	246	5.27	0.635	66.0	70.9	3.9	0.195	0.021
84	246	5.27	0.635	61.0	66.9	6.0	0.214	0.007
85	246	5.27	0.635	62.8	67.0	5.4	0.216	0.007

Contd.

Peat Sample: Northern Ontario (Contd.)

Exp. Code	Reactor		Feed Concentration % COD	COD Reduction		Rate Change; minutes	K_1 min^{-1}	K_2 min^{-1}
	Temperature °C	Pressure MPa		t = 10 m %	t = 20 m %			
37	260	5.96	0.52	80.8	84.6	6.2	0.219	0.010
45	260	5.96	0.496	71.8	81.9	10.1	0.126	0.0063
54A	260	5.96	0.492	78.7	81.7	6.3	0.216	0.006
54B	260	5.96	0.492	69.5	72.6	6.3	0.168	0.007
98	260	5.96	0.632	62.2	69.4	3.8	0.348	0.028
99	260	5.96	0.632	66.2	71.4	3.8	0.389	0.029
87	260	5.96	0.635	62.8	67.7	3.8	0.233	0.005
86	260	5.96	0.635	65.4	69.0	3.7	0.269	0.009
32	271	6.65	0.557	78.5	81.1	6.0	0.224	0.0047
46	271	6.65	0.496	81.9	84.9	6.6	0.230	0.0195
146	271	6.65	0.7335	61.1	75.1	3.6	0.221	0.0186
147	271	6.65	0.7335	67.7	74.9	3.4	0.304	0.0145
148	271	6.65	0.7335	65.1	71.8	3.8	0.270	0.0130

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Peat Sample: Manitoba

Exp. Code	Reactor		Feed Concentration % COD	COD Reduction		Rate Change; minutes	K_1 min^{-1}	K_2 min^{-1}
	Temperature °C	Pressure MPa		t = 10 m %	t = 20 m %			
5	232	7.27	2.48	74.2	77.3	10.4	0.136	0.0093
6	232	7.27	0.92	71.1	74.7	11.0	0.124	0.0053
4	246	7.27	2.48	77.9	81.5	8.6	0.174	0.0081
19	246	8.23	2.64	84.9	-	8.3	0.189	0.0011
20	246	10.4	3.72	84.5	86.3	7.2	0.193	0.0082
1	260	9.34	0.87	84.6	86.9	7.3	0.273	0.0023
9	260	9.34	2.64	77.5	81.4	5.5	0.260	0.0063
3	260	6.24	0.87	77.0	81.2	5.5	0.258	0.0108
7	271	10.3	0.92	78.3	81.4	5.5	0.260	0.0051
8	271	10.3	2.64	83.3	86.3	5.5	0.323	0.0053

Peat Sample: Newfoundland

Exp. Code	Reactor		Feed Concentration % COD	COD Reduction		Rate Change; minutes	K_1 min^{-1}	K_2 min^{-1}
	Temperature °C	Pressure MPa		t = 10 m %	t = 20 m %			
70A	221	3.72	0.623	50.9	55.3	4.0	0.162	0.0094
70B	221	3.72	0.623	56.7	60.2	3.7	0.188	0.0096
70C	221	3.72	0.623	56.2	60.9	3.8	0.187	0.0098
71A	232	4.58	0.623	58.1	61.5	3.4	0.240	0.0094
71B	232	4.58	0.623	57.8	61.2	3.8	0.217	0.0083
71C	232	4.58	0.623	58.3	62.3	3.4	0.236	0.010
72A	246	5.27	0.623	60.2	64.7	3.6	0.240	0.010
72B	246	5.27	0.623	62.2	66.6	3.8	0.241	0.0090
72C	246	5.27	0.623	59.9	64.2	3.6	0.232	0.011
73A	252	5.62	0.623	60.5	64.7	3.8	0.236	0.0087
73B	252	5.62	0.623	61.5	67.7	3.8	0.242	0.0096
73C	252	5.62	0.623	58.7	65.5	3.8	0.221	0.011
74A	260	5.96	0.623	65.2	68.7	3.7	0.277	0.008
74B	260	5.96	0.623	63.6	69.5	3.7	0.242	0.012
74C	260	5.96	0.623	63.2	66.3	3.7	0.266	0.008
75A	271	6.65	0.623	66.3	69.5	3.6	0.268	0.008
75B	271	6.65	0.623	68.1	69.2	3.8	0.275	0.008
75C	271	6.65	0.623	67.3	70.8	3.4	0.287	0.0095

APPENDIX B

HPLC Analyses of Wet-oxidized Peat Wastewater

Total Oxidation

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Mr. T. Gallo, P.Eng.,
Environmental Chemistry.

February 18, 1982

REPORT NUMBER ACS8-82090

IDENTIFICATION

SPECIFICATIONS OF ORDER Analysis of liquid effluents of WETOX™ treatment of peat by high performance liquid chromatography.

EXPERIMENTAL

Sample Preparation

Two series of samples labelled P-80 and P-81 each with seven individual samples were received. These were shaken to ensure homogeneity and a 1 mL aliquot was removed from each. Each aliquot from the P-80 series was added to the corresponding aliquot from the P-81 series and mixed thoroughly. The combined samples were filtered under gravity (Whatman No. 40 filter paper) and placed in vials for analysis.

Chromatography

The analysis was carried out on a Waters' liquid chromatograph comprising a Waters' WISP automatic sample processer, a Waters' 6000-A pump, a Waters' R401 Refractive Index detector and a Waters' Data Module. The column was a Bio-Rad HPX-87H organic acids analysis column fitted with an Ion Exclusion guard column. Eluent was 0.07 M aqueous H_2SO_4 with a flow

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rate of 0.6 mL/min. The injection volume was 20 µL and the attenuation setting on the refractometer was 2X. External standards of formic and acetic acid of known concentration were used for quantitation.

RESULTS

Quantitations of the four major peaks present in the samples are presented in Table 1. A typical chromatogram is shown in Figure 1. Peak numbers 3 and 4 have been assigned to formic and acetic acids respectively. Peak number 1 has a retention time identical to that of glycollic acid and/or succinic acid. Consideration of the origin of of the sample leads to the conclusion that glycollic acid is more likely to be present in the sample. Peak number 2 has not been assigned. Its chromatographic behavious suggests that it is a di- or tri-basic carboxylic acid or hydroxy acid or polyfunctional alcohol. It is saturated, as evidenced by its lack of strong ultraviolet absorbance at 284 nm. Comparison of retention times indicate that it is not lactic, oxalic, levulinic, glucuromic, citric, tartaric or malic acids. Also it is not one of the alcohols, methanol, ethanol, propanol or butanol. No further work was undertaken to identify this component.

Response factors for formic and acetic acid were calculated and found to be almost identical. This result was then used in quantitations of the other acids. Expression of the results in multiequivalents of acid was based on the known molecular weights of acetic, formic and glycollic acids and on an estimated figure of 100 for the unknown acid.

Discussion

The summed quantitations expressed in milli-equivalents are displayed graphically in Figure 2. Although a molecular weight of 100 was assigned arbitrarily to the unknown component, the small amount of this component means that errors in the total are not large. While the deduction of these figures involved some estimation, a clear trend

exists which is illustrated in Figure 2. A smooth curve is generated with a maximum centred at sample number 4.

TABLE 1: Quantitation of Organic Acids in Peat Extracts

Sample No.	Acid (milli-equivalents/litre)				Total	t
	glycollic mw 76	Unknown *mw 100	Formic 46	Acetic 60		
1	0.66	0.0	1.30	3.17	5.13	0
2	2.11	0.9	7.17	4.83	15.01	3
3	1.84	0.9	8.04	6.00	16.78	6
4	2.11	0.7	7.17	7.20	17.18	10
5	2.11	0.8	6.09	8.00	17.00	15
6	2.37	0.7	5.22	8.00	16.29	20
7	2.37	0.5	2.83	8.83	14.53	40

* molecular weight arbitrarily assumed to be 100

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Department of Applied Chemistry

DLM:EL

ACS8-82090

Fig 1.

Peat Extracts
Sample # 4

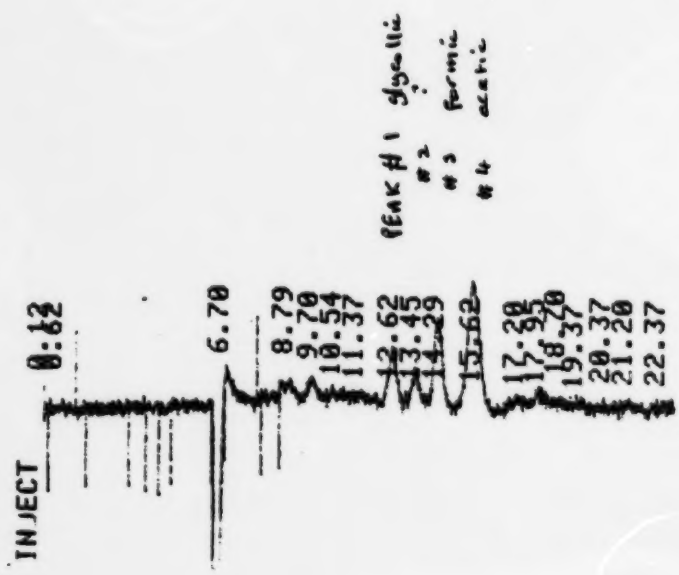
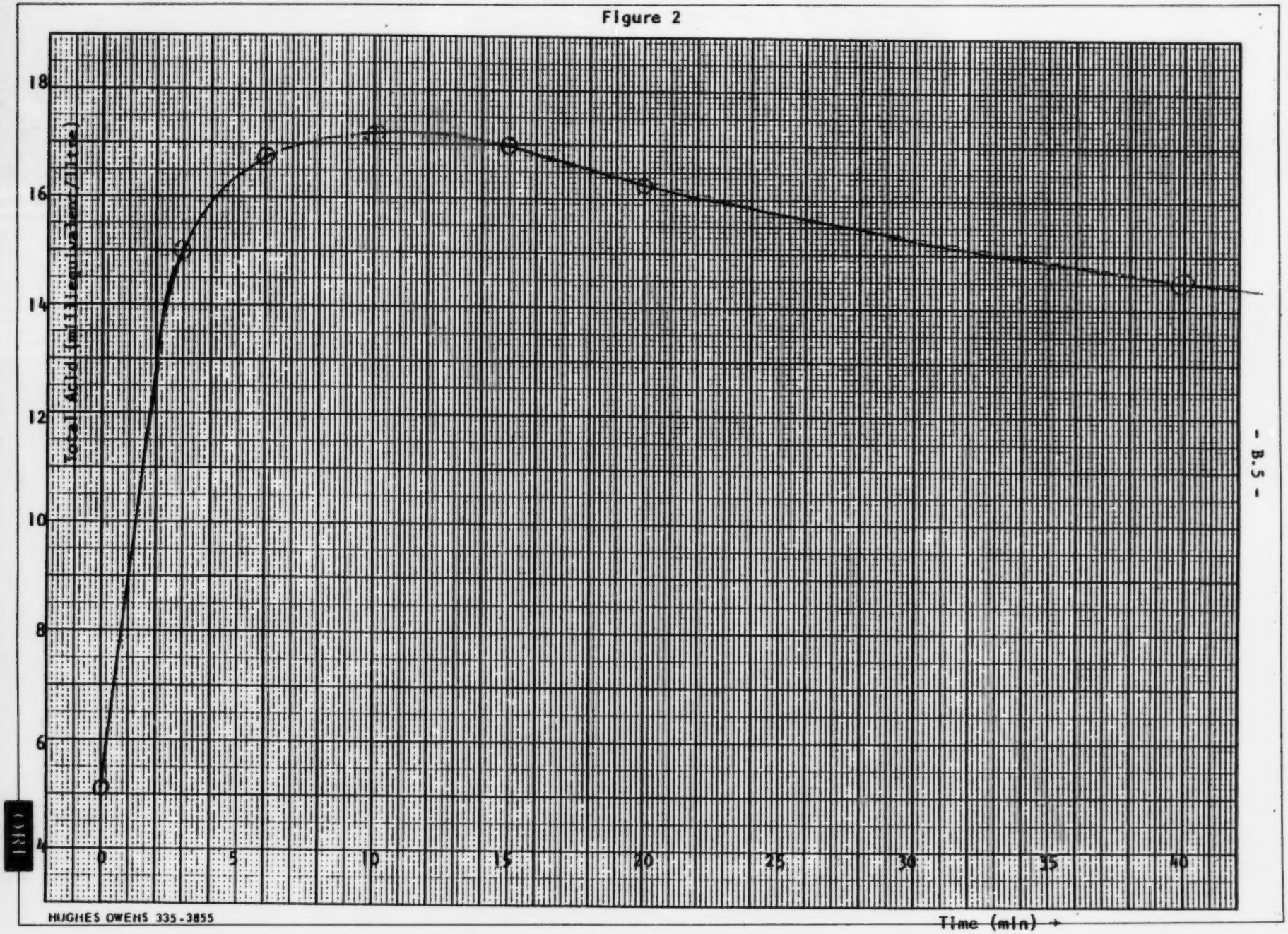


Figure 2


Total Acid (milliequivalents/litre)
18
16
14
12
10
8
6
4
0
5
10
15
20
25
30
35
40
Time (min) →
HUGHES OWENS 335-3855

APPENDIX C

Partial Oxidation Data

TABLE C.1 - Partial Oxidation of Northern Ontario Peat
At 163°C, 9.6% Stoichiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	147.4	100	0.2		92.8	98.8			79.1	10.8	79.5
0	145.1	98.4	12.9	8.9	86.7	93.2			67.1	12.7	77.5
5	128.0	93.1	21.5	16.8	75.8	81.3			45.1	14.5	78.5
10	136.0	96.1	21.5	15.8	80.4	86.5	21.61	92.5	50.8	13.9	78.0
15	149.0	92.3	20.0	13.4	80.9	87.0			49.3	14.0	77.0
20	143.0	97.0	22.7	15.9	76.4	82.2			48.6	14.2	79.4
40	130.2	88.3	21.5	16.5	75.8	81.5			43.6	15.0	75.5

ORI

TABLE C.2 - Partial Oxidation of Northern Ontario Peat
At 163°C, 12.6% Stoichiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	147.4		0.2		92.8	99.8			74.9	10.8	79.5
0	145.1	98.4	12.9	8.9	86.7	93.2			67.1	12.7	77.5
5	133.0	90.2	13.7	10.3	87.5	94.1			67.9	13.1	79.1
10	126.0	85.5	18.2	14.4	77.7	83.6	NA	NA	60.3	11.3	79.0
15	130.0	88.2	18.5	14.2	89.2	95.9			59.3	14.0	75.9
20	130.0	88.2	20.0	15.4	81.3	87.1			60.3	14.2	76.3
40	130.0	88.2	22.3	17.2	86.5	93.0			53.4	14.1	74.7

TABLE C.3 - Partial Oxidation of Northern Ontario Peat
At 163°C, 15.7% Stoichiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	147.4	100	0.2		92.8	99.8			74.9	10.8	79.5
0	145.1	98.4	12.9	8.9	86.7	93.2			67.9	12.7	77.5
5	131.0	88.9	14.6	11.2	83.6	89.9			66.4	13.1	78.3
10	130.0	88.2	17.5	13.5	81.8	88.0	21.82	94.9	66.6	13.5	74.8
15	130.0	88.2	18.4	14.2	85.5	91.9			60.8	14.0	75.4
20	129.3	87.7	20.8	16.1	86.3	92.8			56.7	13.3	74.9
40	120.5	81.8	23.0	19.1	83.2	89.5			55.4	13.4	73.8

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TABLE C.4 - Partial Oxidation of Northern Ontario Peat
At 163°C, 20% Stoichiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	147.4	100	0.2		92.8	99.8			74.9	10.8	79.5
0	145.1	98.4	12.9	8.9	86.7	93.2			67.1	12.7	77.5
5	138.2	93.8	15.2	11.0	87.0	93.5			69.4	13.3	77.8
10	137.5	93.3	16.5	12.0	87.8	94.4	21.03	98.2	61.4	14.3	78.5
15	131.0	88.9	22.8	17.8	73.7	79.2			62.8	15.8	76.1
20	133.5	90.6	22.3	16.7	85.0	91.4			56.8	14.5	79.4
40	137.0	92.9	24.3	17.7	78.1	84.0			54.1	15.2	72.4

TABLE C.5 - Partial Oxidation of Northern Ontario Peat
At 163°C, 25% Stoichiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	147.4	100	0.2		92.8	99.8			74.9	10.8	79.5
0	145.1	98.4	12.9	8.9	86.7	93.2			67.1	12.7	77.5
5	148.0	100+	14.6	9.9	88.1	94.7			68.7	13.8	77.8
10	126.4	85.8	16.0	12.7	82.6	88.8	20.90	91.8	66.6	13.5	78.5
15	129.0	87.5	21.5	14.6	87.7	94.3			62.0	14.8	76.1
20	129.6	87.9	23.1	15.7	85.1	91.5			58.1	15.2	79.4
40	128.2	86.9	26.9	18.3	84.2	90.5			52.7	14.9	72.4

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TABLE C.6 - Partial Oxidation of Northern Ontario Peat
At 177°C, Nitrogen Atmosphere

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
0	129.0	87.5	10.4	8.1	61.5	66.1	22.15	72.4	47.8	14.4	79.2
5	118.6	80.5	15.9	13.4	64.9	69.8	21.73	75.0	50.1	14.3	75.2
10	126.0	85.5	16.3	12.9	71.4	76.8	22.09	83.9	50.2	14.8	76.8
15	123.0	83.4	15.5	12.6	70.8	76.1	20.59	77.5	51.2	14.6	72.1
20	122.0	82.8	17.2	14.1	65.1	70.0	20.88	72.3	50.8	13.2	78.0

TABLE C.7 - Partial Oxidation of Northern Ontario Peat
At 177°C, 15% Stiochiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	161.8	100	0.30		114		20.22		74.1	108	
5	156.9	97.0	23.1	14.7	105.2	91.5			52.5	13.4	78.3
10	145.8	90.1	24.6	16.9	95.7	83.2	21.70	89.3	42.2	21.5	74.8
15	141.9	87.7	24.3	17.1	93.4	81.2			47.9	16.7	75.4
20	139.2	86.0	23.8	17.1	92.0	80.0			48.4	15.7	74.9
40	139.2	86.0	23.1	16.6	83.5	72.6			41.8	20.8	73.8

ORI

TABLE C.8 - Partial Oxidation of Nothern Ontario Peat
At 177°C, 20% Stoichiometric Oxygen

Time min	TCOD		SCOD		SS		Heating Value		Pressed Cake		Filter Cake % H_2O
	g/L	% of Feed	g/L	% TCOD	g/L	% Recovery of TSS	MJ/kg dry	% Recovery	% H_2O	% Ash	
Raw	147.4	100	0.2		92.8	99.7	20.22		74.9	10.8	79.5
0	127.0	86.2	12.4	9.8	76.3	82.0	18.73	75.0	49.7	14.0	78.6
5	138.8	94.8	22.3	16.1	70.8	76.1	18.78	70.7	47.0	15.5	77.7
10	129.0	87.5	24.8	19.2	72.3	77.7	19.69	75.7	39.8	15.8	74.8
20	135.3	91.8	23.8	17.6	78.3	84.2	19.08	79.4	41.7	16.3	75.2
40	122.5	83.1	23.8	19.5	77.4	83.2	19.14	78.8	39.8	14.9	73.9

APPENDIX D

WETXT 2 Program Listing
Program simulates mass, energy and
economic balance of Cases 1 and 2

```
00100 MACHINE,A.
00200 NRC,CM100000,T100,P3.
00300 USER,A268061.
00400 *
00500 * JOB,WETXT2
00600 *
00700 ROUTE,OUTPUT,DEF,MID=B,PF=WETEMP.
00710 ROUTE,XOUT,DEF,MID=B,PF=DAYI
00800 FTN,R=0,L=0,OPT=0,A.
00810 REPLACE,LGO=ETHIC
00900 LDSET,PRESET=ZERO
01000 LOAD,LGO.
01010 EXECUTE
01100 GOTO,IA.
01200 EXIT.
01300 IA,DAYFILE,XOUT.
01305 CATLIST,LO=F.
01400 7/8/9
01410       PROGRAM WETOXT(INPUT=400B,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
01420 C     PROGRAM TO EVALUATE A WETOX PLANT FOR THE PRODUCTION
01430 C     OF STEAM, HOT WATER, METHANE AND/OR ELECTRICITY
01432 C     FROM WET MINED PEAT
01435 C
01440       REAL K101,K102,KA,KB,L10,MF,IR,LIFE,LNC,LNVP,K1,K2,L9,LFAC,
01442      $LCT11,KWP,KWC
01450       NAMELIST/VARS/K101,K102,KA,KB,T10,RT10,CODIN,PL10,EXSA,
01460      $TINI,OVP,FR10,MF,L10,NSTEP,UHEX1,HR,ELEC,DRT,DCOD,DTEM,DRM,BP,
01470      $IR,LIFE,RM,ITEMP,ICOD,IRT,K1,K2,L9,VN9,B9A,B9B,B9C,WALL,ROOF,PL9,
01472      $IRM,T9,SSA,DEAD,LFAC,TREAT,RECYC,H2DR,TAMB,NR9
01480       READ(5,VARS)
01490     5 FORMAT('1    INPUT VARIABLES')
01500       WRITE(6,VARS)
01510       NAMELIST/OPTS/IFLTH,IFLCD,IFLRT,IFLRM,IFLAD,IFLEG
01520       READ(5,OPTS)
01530       WRITE(6,10)
01540    10 FORMAT(1H1,"      INPUT OPTIONS")
01550       WRITE(6,OPTS)
01560       WRITE(6,12)
01562       WRITE(6,14)
01564       IF(IFLEG EQ 1) WRITE(6,16)
01566       IF(IFLEG EQ 0) WRITE(6,17)
01568       WRITE(6,18)
01570    12 FORMAT(1H1,3X,"PEAT      COD     RES     REAC          OPER    WETOX
01572      $ CAP          COD     THERM.     NET          ENERGY")
01574    14 FORMAT(4X,"COST     CONC.    TIME    TEMP          COST     COST     COS
01576      $T        REMOV.   EFFIC.    POWER          COST")
01578    16 FORMAT(3X,"($/T)     (G/L)   (MIN)     (C)        ($/HR)    (M$)     (M$
01580      $)          (%)       (%)     (MW)         ($/KWH)")
01582    17 FORMAT(3X,"($/T)     (G/L)   (MIN)     (C)        ($/HR)    (M$)     (M$
01590      $)          (%)       (%)     (MW)         ($/GJ)")
01592    18 FORMAT(3X,"=============================================================
01594      $=============================================")
01600       LINE = 0
01620 C
01630 C     COD REMOVAL SECTION
01640 C
01690 C     ARRHENIUS EQUATION AND TEMP LOOP
01700 C
01702       VP = 760
01705       T10A = T10
```

```
01710         DO 130 I=1,ITEMP
01720         RCT = -0.063*T10A+21.8
01730         T10AK = T10A+273
01740         K101 = KA*2.71828**(KB/(1.986*T10AK))
01750 C
01760 C       START COD LOOP
01770 C
01780         CODA = CODIN
01790         DO 120 J=1,ICOD
01810 C
01820 C       START TIME LOOP
01830 C
01840         RT10A = RT10
01850         DO 110 K=1,IRT
01870 C
01880 C       CALCULATES COD REMOVAL
01890 C
01900         IF(RT10A.LE.RCT) RCT = RT10A
01910         LNC = ALOG(CODA)-K101*RCT-K102*(RT10A-RCT)
01920         COD1 = 2.71828**LNC
01930         CODL = CODA*FR10/1000
01940         CODR = (CODA-COD1)/CODA
01945         CODRP = CODR*100
01950 C
01960 C       WASTETREATMENT COST
01970 C
01975         IF(IFLAD.EQ.1) PL10 = 0
01980         POL10 = PL10*COD1*FR10/1000.
01990 C
02000 C       AIR REQUIRED
02010 C
02020         AIRF = (EXSA+1)*CODL*CODR/0.23
02030         AIRV = AIRF/0.00115
02040 C
02050 C       STEAM PRESSURE
02060 C
02070         T10AK = T10A+273
02090         DO 40 IVP=1,4
02100         LNVP = 55.336-6869.5/T10AK-5.115*ALOG(T10AK)+1.03*VP/T10AK**2
02110         VP = 2.71828**LNVP
02120    40   CONTINUE
02130 C
02140 C       HEAT OF VAPOURIZATION
02150 C
02160         HVAP = 1913.3*((1-T10AK)/(1-478))**0.38
02170 C
02180 C       STEAM PRODUCTION
02190 C
02200         VPP = VP*0.0001333
02210         RPR = VPP*(1+OVP)
02220         STMF = (AIRF*0.622*VPP)/(RPR-VPP)
02230 C
02240 C       STEAM ENTHALPY
02250 C
02260         HSTM = HVAP*STMF+T10A*4.1738*STMF
02270 C
02280 C       LIQUID EFFLUENT FLOW AND ENTHALPY
02290 C
02300         FR11 = FR10-STMF
02310         HLIQ = FR11*T10A*4.1738
```


ORI

```
02320 C
02330 C      OFF GAS ENTHALPY
02340 C
02350        HGAS = 1.027*(T10A-177)*AIRF
02360 C
02370 C      HEAT OF REACTION
02380 C
02390        HOX = CODL*CODR*13923
02400 C
02410 C      PREHEAT TEMPERATURE REQUIRED
02420 C      AND HEAT EXCHANGER DUTY
02430 C
02440        HIN = HSTM+HGAS+HLIQ-HOX
02450        TIN2 = HIN/(FR10*4.1738)
02460        HEX1 = (TIN2-TIN1)*FR10*4.1738
02470        IF(TIN2.GE.T10A) GO TO 104
02480        IF(IFLEG.EQ.1) HEX1 = 0.
02490 C
02500 C      NET THERMAL OUTPUT
02510 C
02520        HNET = HSTM+HLIQ-HEX1-32.*FR10*4.1738
02530        IF(HNET.LE.0) WRITE(6,50)
02540   50   FORMAT(14X,22HINSUFFICIENT HEAT GAIN)
02560 C
02570 C      PUMPING POWER AND COST
02580 C
02590        KWP = RPR*FR10*0.2784
02600        PCST = 0.00117*FR10**0.45
02610 C
02620 C      COMPRESSOR POWER AND COST
02630 C
02640 C      3-STAGES REQUIRED
02650 C
02660        IF(RPR+0.344.LE.5.15) GO TO 55
02670        RATIO = ((RPR+0.344)/0.101)**0.094-1
02680        KWC = 0.4*AIRV*RATIO
02682        T2 = (RATIO+1.)*303.-273.
02684        CHEAT = 1.027*2.*AIRF*(T2-10.)
02700        CCST = 0.00248*AIRV**0.51
02710        GO TO 60
02715   55   CONTINUE
02720 C
02730 C      2-STAGES REQUIRED
02740 C
02750        RATIO = ((RPR+0.344)/0.101)**0.142-1
02760        KWC = 0.267*AIRV*RATIO
02762        T2 = (RATIO+1.)*303.-273.
02764        CHEAT = 1.027*AIRF*(T2-10.)
02770        CCST = 0.00191*AIRV**0.53
02780   60   CONTINUE
02830 C
02840 C      REACTOR VOLUME AND COST
02845 C
02850        TVOL = FR10*RT10A/60.
02860        RNM = TVOL/16.
02870        INM = INT(RNM)+1
02880        VOL = TVOL/INM
02890        RCST = MF*0.37*(TVOL*RPR/73.12)+0.09*INM
02900 C
02910 C      HEAT TRANSFER AREA REQUIRED
```

```
02920 C
02930       T11 = T10A
02940       IF(HEX1.GT.HVAP*STMF) T11=T10A-(HEX1-(HVAP*STMF))/(FR10*4.1738)
02945       IF(T11.LE.0) GO TO 105
02950       DT1 = T10A-TIN2
02960       DT2 = T11-TIN1
02970       LMTD = (DT2-DT1)/ALOG(DT2/DT1)
02980       AHEX1 = HEX1/(LMTD*UHEX1)
02990 C
03000 C     HEAT EXCHANGER COST
03010 C
03020       HCST = MF*0.0035*AHEX1**0.61
03030 C
03040 C     LABOUR REQUIRED AND COST
03050 C
03060       LR10 = (L10/NSTEP*FR10)/(24*FR10)**0.76
03070       LCT10A = 1.9*LR10*HR
03080 C
03120 C     ------------------------------------------------------------
03130 C
03140 C     ANAEROBIC DIGESTION
03150 C
03160 C     CHECKS FLAG
03170 C
03180       IF(IFLAD.EQ.0) GO TO 65
03240 C     CALCULATE COD LOAD
03250 C
03255       COD1W = COD1*FR10/1000
03260       COD2 = COD1W*24000
03270 C
03280 C
03290 C     REACTOR DESIGN
03300 C
03310       INUM = 1
03320       RVOL1 = COD2/LFAC
03330       VOID = 65/SSA
03340       RVOL2 = RVOL1/VOID
03350       IF(RVOL2.GT.1000) INUM = RVOL2/1000 +1
03360       RVOL3 = RVOL2/INUM
03370       RAD1 = (RVOL3/(6.283*H2DR))**0.333
03380       HGHT1 = RAD1*2*H2DR
03390       HGHT2 = HGHT1*(1+DEAD)
03400       RVOL4 = 3.1416*RAD1**2*HGHT2
03410       SSAR = SSA*RVOL3/RVOL4
03420       RVOL5 = RVOL4*1.1*INUM
03430 C
03440 C
03450 C     CALCULATE COD REMOVAL EFFICIENCY
03460 C
03470       TFAC = (0.557*T9-1.546)/18
03480       IF(SSAR.LT.83) MAXLR = (4.04+0.036*SSAR)*TFAC
03490       IF(SSAR.GE.83) MAXLR = (0.297*SSAR-17.68)*TFAC
03500       EFF = TREAT
03520       RMEF = (MAXLR-LFAC)*0.00647+(0.84*EFF)
03530 C
03540 C     CALCULATE RESIDENCE TIME
03550 C
03610       RRES = (RVOL2/FR10)/24
03620 C
03630 C
```

CORE1

```
03440 C      CALCULATE HEAT LOSS
03450 C
03460         LOSS = (6.283*K1*HGHT2*(T9-TAMB)/(ALOG((RADI+WALL)
03470        $/RADI))+6.283*RADI**2 *K2*(T9-TAMB)/ROOF)*INUM
03480         DELTA = LOSS/((FR10*4.1736)
03490         TEFF = T9-DELTA
03500 C
03510 C
03520 C      PUMPING REQUIRED AND COST
03530 C
03540         ER9 = FR10*(RECYC+1.)*0.002722*HGHT2
03550         EC9 = ER9*ELEC
03560 C
03570 C
03580 C      WASTE TREATMENT COST
03590 C
03600         FOLU9 = FL9*CODIW*(1.-RMEF)
03610         ECOD  = FOLU9/FL9
03620 C
03630 C
03640 C      CALCULATE GAS PRODUCTION
03650 C
03660         GP = (CODIW-ECOD)*0.35*24000.
03670 C
03680 C
03690 C      NUTRIENTS REQUIRED AND COST
03700 C
03710         CHEM9 = NR9*(CODIW-ECOD)
03720         CC9 = VN9*CHEM9
03730 C
03740 C
03750 C      LABOUR REQUIRED AND COST
03760 C
03770         LR9 = (L9/NSTEP*GP/33487.)/(24.*GP/33487.)**0.74
03780         LCT9 = 1.9*LR9*HR
03790 C
04000 C
04010 C      TOTAL OPERATING COST
04020 C
04030         TOC9 = EC9+CC9+LCT9+FOLU9
04040 C
04050 C
04060 C      ENERGY RECOVERY
04070 C
04080         ERC9 = GP*1.44
04090 C
04100 C      CALCULATE CAPITAL COSTS
04101 C
04102         CR9A = B9A*INUM*(FR10*(1.+RECYC)*HGHT2/INUM)**0.5
04103         CR9B = B9B*RVOL2
04104         CR9C = B9C*RVOL4**0.6*INUM
04105         CR9 = CR9A+CR9B+CR9C
04120         GO TO 70
04122 C
04124 C      NO ANAEROBIC DIGESTION
04126 C
04127    65   CONTINUE
04128         CR9=ER9=ERC9=TOC9=0
04129    70   CONTINUE
04130 C
```

```
04132 C     THERMAL POWER OUTPUT
04133 C
04134       IF(IFLEG.EQ.1) TMJ = 0
04135       PWR = 2.778E-4*(HNET+ERC9+CHEAT)
04136       PWRN = PWR
04137 C     ------------------------------------------------------------
04138 C     ELECTRICAL GENERATION
04140 C     CHECKS FLAG
04142 C
04144       IF(IFLEG.EQ.0) GO TO 80
04146 C
04150       IF(IFLAG.EQ.0) GO TO 72
04160       EEFF = 0.172*ERC9/(0.24*HNET)
04170       IF(ERC9.GE.0.24*HNET) EEFF = 0.172
04180       GO TO 75
04190    72 CONTINUE
04195       EEFF = 0.128
04200    75 CONTINUE
04210       EGEN = EEFF*PWR-(KWC+KWP)/1000.
04212       EGEN2 = EEFF*PWR
04215       PWRN = EGEN
04220       ELCST = 1.5*(EGEN2/10.)**0.6
04230       LCTII = 0.0.?*EGEN2*(1000./EGEN2)**0.74
04232       GO TO 85
04234 C
04236 C     NO ELECTRICAL GENERATION
04238 C
04240    80 CONTINUE
04242       LCTII=ELCST=0
04244    85 CONTINUE
04246 C
04250 C
04260 C
04265 C
04270 C     THERMAL EFFICIENCY
04275 C
04280       IF(IFLEG.EQ.1) GO TO 90
04285       HTOT = (HNET+ERC9)
04290       TMJ = 10.8*(KWC+KWP+ER9)
04295       THEF = HTOT/(TMJ+CODL*13923.)
04297       GO TO 95
04299    90 CONTINUE
04300       THEF = ((HNET+ERC9)*EEFF-3.6*(KWC+KWP+ER9))/(CODL*13923.)
04302    95 CONTINUE
04303       THEFP = THEF*100
04304 C
04370 C
04380 C     INSTALLED PLANT COST
04390 C
04400       TCCST = (CCST+PCST+RCST+MCST+CR9+ELCST)*BP
04410 C
04420 C     MAINTENANCE COST
04430 C
04440       MCST = 0.05*TCCST/87.0
04450 C
04460 C     TOTAL OPERATING COSTS
04470 C
04480       IF(IFLEG.EQ.1) ELEC = 0
04490       ENER = (KWC+KWP+ER9)*ELEC
04500       OCST = LCTIOA+ENER+POLIO+MCST+TOC9+LCTII
```

```
04510 C
04520 C      INVESTMENT COST ANALYSIS USING CAPITAL RECOVERY FACTOR
04530 C
04540        VCST1 = TCCST+(2190*OCST)
04550        VCST2 = VCST1*(IR*(1+IR)**LIFE)/((1+IR)**LIFE-1)
04560        VCST3 = VCST2/8760
04570 C
04580 C      RAW MATERIAL COST LOOP
04590 C
04600        RMA = RM
04610        DO 102 L=1,IRM
04620        RMCST = RMA*FR10
04630 C
04640 C      ENERGY PRODUCTION COST
04650 C
04670        ECST = 1000*(VCST3+RMCST+OCST)/(HNET+ERC9)
04675        IF(IFLEG.EQ.1) ECST = (VCST3+RMCST+OCST)/(EGEN*1000)
04680 C
04690 C      PRINT OUT RESULTS
04700 C
04702        IF(LINE.NE.56) GO TO 97
04704        WRITE (6,12)
04706        WRITE(6,14)
04708        IF(IFLEG.EQ.1) WRITE(6,16)
04710        IF(IFLEG.EQ.0) WRITE(6,17)
04712        WRITE(6,18)
04714        LINE = 0.
04716    97  CONTINUE
04717        IF(ECST.LE.0) GO TO 101
04718        PRINT 100,RMA,CODA,RT10A,T10A,OCST,RCST,TCCST,CODRP,THEFF,
04719       $PWRN,ECST
04720   100  FORMAT(3X,F5.2,4X,F5.1,2X,F5.1,3X,F5.1,6X,F6.2,2X,F5.2,3X,F5.1,
04722       $7X,F5.2,4X,F5.1,4X,F4.1,6X,F7.3)
04723        GO TO 103
04724   101  PRINT 109,RMA,CODA,RT10A,T10
04725   103  CONTINUE
04726        LINE = LINE+1
04730 C
04740 C      INCREMENT RAW MATERIAL COST
04750 C
04760        IF(IFLRM.EQ.1) RMA = RMA+DRM
04770   102   CONTINUE
04780        GO TO 108
04790   104  CONTINUE
04800        WRITE(6,106) TIN2
04810   105  WRITE(6,50)
04820   106  FORMAT(10X,30HPREHEAT TEMPERATURE TOO HIGH: ,F4.1)
04830   108  CONTINUE
04835   109  FORMAT(3X,F5.2,4X,F5.1,2X,F5.1,3X,F5.1,6X,
04836       $"NO NET POWER AVAILABLE")
04840 C
04850 C      INCREMENT VARIABLES
04860 C
04870        IF(IFLRT.EQ.1) RT10A = RT10A+DRT
04880   110  CONTINUE
04890        IF(IFLCD.EQ.1) CODA = CODA+DCOD
04900   120  CONTINUE
04910        IF(IFLTH.EQ.1) T10A = T10A+DTEM
04920   130  CONTINUE
04930        STOP 5555
```

```
04940        END
04950 7/8/9 NS
04960  $VARS
04970  K101=0.0, K102=0.01, KA=4111 , KB=-10401 , T10=232.2, RT10=5 ,
04980  CODIN=50., RM=0.4, PL10=254., EXSA=0.1, TINI=10 , OVP=0.5,
04990  FR10=50 , MF=1.0, L10=19, NSTEP=1., UHEX1=0.204, HR=10.,
05000  ELEC=0.05, DRT=7.5, DCOD=50 , DTEM=19.4, DRM=1.1, BP=3., IR=0.18, LIFE=20 ,
05010  ITEMP=3, ICOD=3, IRT=5, IRM=5,
05020  K1=2.74E-3, K2=1.37E-4, L9=19., VN9=220., B9A=5.55E-5, B9B=1.0E-4,
05030  B9C=4.75E-3, WALL=0.5, ROOF=0.15, PL9=254., T9=30 , SSA=75 , DEAD=0.1,
05040  LFAC=12 , TREAT=0.8, RECYC=2., H2DR=1., TAMB=18., HR9=0.2438,
05050  $
05060  $OPTS
05070  IFLTM=1, IFLCD=1, IFLRT=1, IFLRM=1, IFLAD=1, IFLEG=0,
05080  $
```


ORI

APPENDIX E

WETX 4 Program Listing
Program simulates mass, energy and
economic balance of Case 3

```
00100 MACHINE,A.
00200 NRC,CM100000,T100,P3.
00300 USER,A248081.
00400 *
00500 * JOB,WETX4
00600 *
00700 ROUTE,OUTPUT,DEF,MID=B,PF=WETOUT.
00710 ROUTE,XOUT,DEF,MID=B,PF=DAYI.
00800 FTN,R=0,L=0,OPT=0,A.
00810 REPLACE,LGO=ETHIC.
00900 LDSET,PRESET=ZERO.
01000 LOAD,LGO.
01010 EXECUTE.
01100 GOTO,IA.
01200 EXIT.
01300 IA,DAYFILE,XOUT.
01305 CATLIST,LO=F.
01400 7/8/9
01410       PROGRAM WETOX4(INPUT=400B,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
01420 C     PROGRAM TO EVALUATE A WETOX PLANT FOR THE PARTIAL OXIDATION
01430 C     AND SUBSEQUENT DEWATERING OF FUEL-GRADE WET MINED PEAT.
01435 C
01440       REAL K101,K102,KA,KB,L10,MF,IR,LIFE,LNC,LNVP,K1,K2,L9,LFAC,LCT11
01450       NAMELIST/VARS/K102,KA,KB,T10,RT10,CODIN,PL10,EXSA,
01460      $TIN1,OVP,FR10,MF,L10,NSTEP,UHEX1,HR,ELEC,DRT,DCOD,DTEM,DRM,BP,
01470      $IR,LIFE,RM,ITEMP,ICOD,IRT,K1,K2,L9,VN9,B9A,B9B,B9C,WALL,ROOF,PL9,
01472      $IRM,T9,SSA,DEAD,LFAC,TREAT,RECYC,H2DR,TAMB,NR9,SOLU,SREC
01480       READ(5,VARS)
01500       WRITE(6,VARS)
01510       NAMELIST/OPTS/IFLTM,IFLCD,IFLRT,IFLRM,IFLAD,IFLEC
01520       READ(5,OPTS)
01550       WRITE(6,OPTS)
01540       WRITE(6,12)
01542       WRITE(6,14)
01544       IF(IFLEC.EQ.1) WRITE(6,16)
01546       IF(IFLEC.EQ.0) WRITE(6,17)
01548       WRITE(6,18)
01570   12  FORMAT(1H1,3X,"PEAT      COD      RES.    REAC.         STEAM    HEAT
01572      $ GAS          PEAT     MOIST.   CAPITAL    PEAT         ENERGY")
01574   14  FORMAT(4X,"COST     CONC.     TIME    TEMP           REQU.    OUT      PRO
01576      $D.        PROD.     CONT.    COST      COST          COST")
01578   16  FORMAT(3X,"($/T)     (G/L)   (MIN)     (C)          ($/HR)    (M$)     (M$
01580      $)           (%)       (%)     (MW)          ($/KWH)")
01582   17  FORMAT(3X,"($/T)     (G/L)   (MIN)     (C)          (T/HR) (GJ/HR)   (GJ/
01590      $HR)       (T/HR)     (%)       (M$)     ($/T)        ($/GJ)")
01592   18  FORMAT(3X,"-----------------------------------------------------
01594      $-----------------------------------------------------")
01600       LINE = 0.
01620 C
01630 C     COD REMOVAL SECTION
01640 C
01690 C     ARRHENIUS EQUATION AND TEMP LOOP
01700 C
01702       VP = 760.
01704       K101 = 0.0315
01705       T10A = T10
01706       CLNST = 0
01708       HREQ = 0
01710       DO 130 I=1,ITEMP
01720       RCT = -0.063*T10A+21.8
```

```
01730         T10AK = T10A+273.
01750 C
01760 C       START COD LOOP
01770 C
01780         CODA = CODIN
01790         DO 120 J=1,ICOD
01795         CODB = CODA
01810 C
01820 C       START TIME LOOP
01830 C
01840         RT10A = RT10
01850         DO 110 K=1,IRT
01870 C
01880 C       CALCULATES COD REMOVAL
01890 C
01892         DO 45 ISTM = 1,5
01894         FR10B = FR10
01896         FR10B = FR10B+CLNST
01898         CODB = CODA*FR10/FR10B
01900         IF(RT10A.LE.RCT) RCT = RT10A
01910         LNC = ALOG(CODB)-K101*RCT-K102*(RT10A-RCT)
01920         COD1 = 2.71828**LNC
01925         SCOD1 = COD1*SOLU
01930         CODL = CODB*FR10B/1000.
01940         CODR = (CODB-COD1)/CODB
01945         CODRP = CODR*100.
01950 C
01960 C       WASTETREATMENT COST
01970 C
01975         IF(ISLAD.EQ.1) PL10 = 0.
01980         POL10 = PL10*COD1*FR10B/1000.
01990 7
02000 C       AIR REQUIRED
02010 C
02020         AIRF = (EXSA+1)*CODL*CODR/0.23
02030         AIRV = AIRF/0.00115
02040 C
02050 C       STEAM PRESSURE
02060 C
02070         T10AK = T10A+273.
02090         DO 40 IVP=1,6
02100         LNVP = 55.336-6869.5/T10AK-5.115*ALOG(T10AK)+1.05*VP/T10AK**2
02110         VP = 2.71828**LNVP
02120    40   CONTINUE
02130 C
02140 C       HEAT OF VAPOURIZATION
02150 C
02160         HVAP = 1913.3*((1-T10AK)/(1-478))**0.38
02170 C
02180 C       STEAM PRODUCTION
02190 C
02200         VPP = VP*0.0001333
02210         RPR = VPP*(1+OVP)
02220         STMF = (AIRF*0.622*VPP)/(RPR-VPP)
02230 C
02240 C       STEAM ENTHALPY
02250 C
02260         HSTM = HVAP*STMF+T10A*4.1736*STMF
02270 C
02280 C       LIQUID EFFLUENT FLOW AND ENTHALPY
```

```
02290 C
02300       FR11 = FR10B-STMF
02310       HLIQ = FR11*T10A*4.1738
02320 C
02330 C     OFF GAS ENTHALPY
02340 C
02350       HGAS = 1.027*(T10A-177)*AIRF
02360 C
02370 C     HEAT OF REACTION
02380 C
02390       HOX = CODL*CODR*13923
0240 C
02410 C     PREHEAT TEMPERATURE REQUIRED
02420 C     AND HEAT EXCHANGER DUTY
02430 C
02440       HIN = HSTM+HGAS+HLIQ-HOX
02450       TIN2 = HIN/(FR10B*4.1738)
02460       HEX1 = (TIN2-TIN1)*FR10*4.1738/0.85
02465       CLNST = HEX1/2785.
02468    45 CONTINUE
02470       IF(TIN2.GE.T10A) GO TO 104
02480       IF(IFLEG.EQ.1) HEX1 = 0
02490 C
02500 C     NET THERMAL OUTPUT
02510 C
02520       HNET = HSTM+HLIQ-HEX1-32*FR10B*4.1738
02530       IF(HNET.LE.0) HREQ = -HNET
02540       IF(HNET.LE.0) HEX1 = HNET+HEX1+FR10B*57*4.1738
02550       HNETG = HNET/1000.
02560 C
02570 C     PUMPING POWER AND COST
02580 C
02590       KWP = RPR*FR10*0.2784
02600       PCST = 0.00117*FR10**0.45
02610 C
02620 C     COMPRESSOR POWER AND COST
02630 C
02640 C     3-STAGES REQUIRED
02650 C
02660       IF(RPR+0.344.LE.5.15) GO TO 55
02670       RATIO = ((RPR+0.344)/0.101)**0.094-1
02680       KWC = 0.4*AIRV*RATIO
02700       CCST = 0.00248*AIRV**0.51
02710       GO TO 60
02715    55 CONTINUE
02720 C
02730 C     2-STAGES REQUIRED
02740 C
02750       RATIO = ((RPR+0.344)/0.101)**0.142-1
02760       KWC = 0.267*AIRV*RATIO
02770       CCST = 0.00191*AIRV**0.53
02780    60 CONTINUE
02830 C
02840 C     REACTOR VOLUME AND COST
02845 C
02850       TVOL = FR10B/60.*RT10A
02860       RNM = TVOL/16
02870       INM = INT(RNM)+1
02880       VOL = TVOL/INM
02890       RCST = MF*(0.37*TVOL/16*RPR/4.57)+0.09*INM
```


ORF

```
02900 C
02910 C     HEAT TRANSFER AREA REQUIRED
02920 C
02930       T11 = T10A
02940       IF(HEX1.GT.HVAP*STMF) T11=T10A-(HEX1-(HVAP*STMF))/(FR10B*4.1738)
02945       IF(T11.LE.0) GO TO 105
02950       DT1 = T10A-TIN2
02960       DT2 = T11-TIN1
02970       LMTD = (DT2-DT1)/ALOG(DT2/DT1)
02980       AHEX1 = HEX1/(LMTD*UHEX1)
02990 C
03000 C     HEAT EXCHANGER COST
03010 C
03020       HCST = MF*0.0035*AHEX1**0.61
03030 C
03040 C     LABOUR REQUIRED AND COST
03050 C
03060       LR10 = (L10/NSTEP*FR10B)/(24*FR10B)**0.76
03070       LCT10A = 1.9*LR10*HR
03072 C
03074 C     SOLIDS RECOVERY
03076 C
03077       TSOUT = SREC*CODL/1.4
03078       HOUT = TSOUT*21.8
03080 C
03120 C     ************************************************************
03130 C
03140 C     ANAEROBIC DIGESTION
03150 C
03160 C     CHECKS FLAG
03170 C
03180       IF(IFLAD.EQ.0) GO TO 65
03240 C     CALCULATE COD LOAD
03250 C
03252       FR10B = FR10B*(1-(CODB/1570.))
03255       CODIW = SCOD1*FR10B/1000.
03260       COD2 = CODIW*24000.
03270 C
03280 C
03290 C     REACTOR DESIGN
03300 C
03310       INUM = 1
03320       RVOL1 = COD2/LFAC
03330       VOID = 65/SSA
03340       RVOL2 = RVOL1/VOID
03350       IF(RVOL2.GT.1000) INUM = RVOL2/1000.+1
03360       RVOL3 = RVOL2/INUM
03370       RAD1 = (RVOL3/(4.283*H2DR))**0.333
03380       HGHT1 = RAD1*2*H2DR
03390       HGHT2 = HGHT1*(1+DEAD)
03400       RVOL4 = 3.1416*RAD1**2*HGHT2
03410       SSAR = SSA*RVOL3/RVOL4
03420       RVOL5 = RVOL4*1.1*INUM
03430 C
03440 C
03450 C     CALCULATE COD REMOVAL EFFICIENCY
03460 C
03470       TFAC = (0.557*T9-1.546)/18.
03480       IF(SSAR.LT.83) MAXLR = (4.04+0.034*SSAR)*TFAC
03490       IF(SSAR.GE.83) MAXLR = (0.297*SSAR-17.68)*TFAC
```

```
03500       EFF = TREAT
03520       RMEF = (MAXLR-LFAC)*0.00667+(0.84*EFF)
03530 C
03540 C     CALCULATE RESIDENCE TIME
03550 C
03610       RRES = (RVOL2/FR10B)/24
03620 C
03630 C
03640 C     CALCULATE HEAT LOSS
03650 C
03660       LOSS = (6.283*K1*HGHT2*(T9-TAMB)/(ALOG((RADI+WALL)
03670      $/RADI))+6.283*RADI**2.*K2*(T9-TAMB)/ROOF)*INUM
03680       DELTA = LOSS/(FR10B*4.1736)
03690       TEFF = T9-DELTA
03700 C
03710 C
03720 C     PUMPING REQUIRED AND COST
03730 C
03740       ER9 = FR10B*(RECYC+1.)*0.002722*HGHT2
03750       EC9 = ER9*ELEC
03760 C
03770 C
03780 C     WASTE TREATMENT COST
03790 C
03800       POLU9 = PL9*CODIW*(1.-RMEF)
03810       ECOD  = POLU9/PL9
03820 C
03830 C
03840 C     CALCULATE GAS PRODUCTION
03850 C
03860       GP = (CODIW-ECOD)*0.35*24000.
03870 C
03880 C
03890 C     NUTRIENTS REQUIRED AND COST
03900 C
03910       CHEM9 = NR9*(CODIW-ECOD)
03920       CC9 = VN9*CHEM9
03930 C
03940 C
03950 C     LABOUR REQUIRED AND COST
03960 C
03970       LR9 = (L9/NSTEP*GP/33487.)/(24.*GP/33487.)**0.76
03980       LCT9 = 1.9*LR9*HR
03990 C
04000 C
04010 C     TOTAL OPERATING COST
04020 C
04030       TOC9 = EC9+CC9+LCT9+POLU9
04040 C
04050 C
04060 C     ENERGY RECOVERY
04070 C
04080       ERC9 = GP*1.66
04085       ERC9G = ERC9/1000
04090 C
04100 C     CALCULATE CAPITAL COSTS
04101 C
04102       CR9A = B9A*INUM*(FR10B*(1.+RECYC)*HGHT2/INUM)**0.5
04103       CR9B = B9B*RVOL2
04104       CR9C = B9C*RVOL4**0.6*INUM
```


ORF

```
04105       CR9 = CR9A+CR9B+CR9C
04120       GO TO 70
04122 C
04124 C     NO ANAEROBIC DIGESTION
04126 C
04127    65 CONTINUE
04128       CR9=ER9=ERC9=TOC9=0.
04129    70 CONTINUE
04130 C
04132 C     THERMAL POWER OUTPUT
04133 C
04134       IF(IFLEG.EQ.1) TMJ = 0.
04135       PWR = 2.778E-4*(HNET+ERC9)
04136       PWRN = PWR
04137 C     ------------------------------------------------------------
04138 C     ELECTRICAL GENERATION
04140 C     CHECKS FLAG
04142 C
04144       IF(IFLEG.EQ.0) GO TO 80
04146 C
04150       IF(IFLAD.EQ.0) GO TO 72
04160       EEFF = 0.172*ERC9/(0.24*HNET)
04170       IF(ERC9.GE.0.24*HNET) EEFF = 0.172
04180       GO TO 75
04190    72 CONTINUE
04195       EEFF = 0.128
04200    75 CONTINUE
04210       EGEN = EEFF*PWR
04215       PWRN = EGEN
04220       ELCST = 1.5*(EGEN/10.)**0.6
04230       LCTII = 0.069*EGEN*(1000./EGEN)**0.76
04232       GO TO 85
04234 C
04236 C     NO ELECTRICAL GENERATION
04238 C
04240    80 CONTINUE
04242       LCTII=ELCST=0.
04244    85 CONTINUE
04246 C
04250 C
04260 C
04265 C
04270 C     THERMAL EFFICIENCY
04275 C
04280       IF(IFLEG.EQ.1) GO TO 90
04285       HTOT = (HNET+ERC9)
04290       TMJ = 10.8*(KWC+KWP+ER9)
04295       THEF = HTOT/(TMJ+CODL*13923.)
04297       GO TO 95
04299    90 CONTINUE
04300       THEF = ((HNET+ERC9)*EEFF-3.6*(KWC+KWP+ER9))/(CODL*13923.)
04302    95 CONTINUE
04303       THEFP = THEF*100
04304 C
04310 C     ------------------------------------------------------------
04312 C
04314 C     DEWATERING CALCULATIONS
04315 C
04318       HDRY = ERC9-HREQ
04320       DWATR = HDRY/3800.
```

```
      FWATR = TSOUT-DWATR
      FTS = 100*FWATR/(FWATR+TSOUT)
C
C     ADDITIONAL CAPITAL COSTS
C
      BCST = 1.61E-3*CLNST**0.37
      DECST = 0.0162*FR10B
      THCST = 0.083*DWATR
C
C     ADDITIONAL ENERGY
C
      ER12 = 7.5*FR10B+14.6*DWATR
C
C     ADDITIONAL LABOUR
C
      LR12 = 10/FR10B+DWATR/8.2
      LCT12 = 1.9*LR12*HR
C=====================================================================
C
C     INSTALLED PLANT COST
C
      TCCST = (CCST+PCST+RCST+HCST+CR9+ELCST+BCST+DECST+THCST)*BP
C
C     MAINTENANCE COST
C
      MCST = 0.05*TCCST/8760
C
C     TOTAL OPERATING COSTS
C
      IF(IFLEG.EQ.1) ELEC = 0.
      ENER = (KWC+KWP+ER9+ER12)*ELEC
      OCST = LCT10A+ENER+POL10+MCST+TOC9+LCT11+LCT12
C
C     INVESTMENT COST ANALYSIS USING CAPITAL RECOVERY FACTOR
C
      VCST1 = TCCST+(2190*OCST)
      VCST2 = VCST1*(IR*(1+IR)**LIFE)/((1+IR)**LIFE-1)
      VCST3 = VCST2/7008.
C
C     RAW MATERIAL COST LOOP
C
      RMA = RM
      DO 102 L=1,IRM
      RMCST = RMA*FR10
C
C     ENERGY PRODUCTION COST
C
      ECST = (VCST3+RMCST+OCST)/HOUT
      PCST = (VCST3+RMCST+OCST)/TSOUT
C
C     PRINT OUT RESULTS
C
      IF(LINE.NE.56) GO TO 97
      WRITE (6,12)
      WRITE(6,14)
      IF(IFLEG.EQ.1) WRITE(6.16)
      IF(IFLEG.EQ.0) WRITE(6.17)
      WRITE(6,18)
      LINE = 0
   97 CONTINUE
```

```
      PRINT 100,RMA,CODA,RT10A,T10A,CLNST,HNETG,ERC9G,TSOUT,FTS,TCCST,
     &PCST,ECST
  100 FORMAT(3X,F5.2,4X,F5.1,2X,F5.1,3X,F5.1,4X,F6.2,2X,F6.1,2X,F6.1,
     &8X,F4.1,4X,F4.1,4X,F5.2,3X,F6.2,5X,F6.2)
      LINE = LINE+1
C
C     INCREMENT RAW MATERIAL COST
C
      IF(IFLRM.EQ.1) RMA = RMA+DRM
  102  CONTINUE
      GO TO 108
  104 CONTINUE
  105 WRITE(6,106) TIN2
  106 FORMAT(10X,30HPREHEAT TEMPERATURE TOO HIGH: ,F4.1)
  108 CONTINUE
C
C     INCREMENT VARIABLES
C
      IF(IFLRT.EQ.1) RT10A = RT10A+DRT
  110 CONTINUE
      IF(IFLCD.EQ.1) CODA = CODA+DCOD
  120 CONTINUE
      IF(IFLTM.EQ.1) T10A = T10A+DTEM
  130 CONTINUE
      STOP 5555
      END
7/8/9 NS
&VARS
 K102=0.01, KA=4111., KB=-10401., T10=204., RT10=10.,
CODIN=50., RM=0.4, PL10=254., EXSA=0.1, TIN1=10., OVP=0.5,
FR10=50., MF=1.0, L10=19, NSTEP=1., UHEX1=0.204, HR=10.,
ELEC=0.05, DRT=5., DCOD=25., DTEM=15., DRM=0.8, BP=3.0, IR=0.18, LIFE=20.,
ITEMP=1, ICOD=5, IRT=1, IRM=6,
K1=2.74E-3, K2=1.37E-4, L9=19., VN9=220., B9A=5.55E-5, B9B=1.0E-4,
B9C=4.75E-3, WALL=0.5, ROOF=0.15, PL9=254., T9=30., SSA=75., DEAD=0.1,
LFAC=12., TREAT=0.8, RECYC=2., H2DR=1., TAMB=18., NR9=0.2438,
SOLU=0.135, SREC=0.616,
&
&OPTS
IFLTM=0, IFLCD=1, IFLRT=0, IFLRM=1, IFLAD=1, IFLEG=0,
&
>RETURN
```

E.8

APPENDIX F

Cost Study, Case 1
Thermal Energy Generation Through
Wet Oxidation and Anaerobic Digestion

```
 $SVARS
 OK101     =  0 0,
 OK102     =   1E-01,
 OKA       =   4111E+04,
 OKB       =  - 10401E+05,
 OT10      =   2322E+03,
 ORT10     =   5E+01,
 OCODIN    =   5E+02,
 OPL10     =   254E+03,
 OEXSA     =   1E+00,
 OTINI     =   1E+02,
 OOVP      =   5E+00,
 OFR10     =   5E+02,
 ONF       =   1E+01,
 OL10      =   19E+02,
 ONSTEP    =  1,
 OUHEXI    =   204E+00,
 OHR       =   1E+02,
 OELEC     =   5E-01,
 ODRT      =   75E+01,
 ODCOD     =   5E+02,
 ODTEM     =   194E+02,
 ODRM      =   11E+01,
 OFP       =   3E+01,
 OIR       =   18E+00,
 OLIFE     =   2E+02,
 ORM       =   4E+00,
 OITEMP    =  3,
 OICOD     =  3,
 OIRT      =  5,
 OK1       =   274E-02,
 OK2       =   137E-03,
 OL9       =   19E+02,
 OVN9      =   22E+03,
 OB9A      =   555E-04,
 OB9B      =   1E-03,
 OB9C      =   475E-02,
 OWALL     =   5E+00,
 OROOF     =   15E+00,
 OPL9      =   254E+03,
 OIRM      =  5,
 OT9       =   3E+02,
 OSSA      =   75E+02,
 ODEAD     =   1E+00,
 OLFAC     =   12E+02,
 OTREAT    =   8E+00,
 ORECYC    =   2E+01,
 OH2DR     =   1E+01,
 OTAMB     =   18E+02,
 ONR9      =  0,
 O$END
 !      INPUT OPTIONS
 I$OPTS
 OIFLTH    =  1,
 OIFLCD    =  1,
 OIFLRT    =  1,
 OIFLRM    =  1,
 OIFLAD    =  1,
 OIFLEC    =  0,
 O$END
```

PEAT COST ($/T)	COD CONC (G/L)	RES TIME (MIN)	REAC TEMP (C)	OPER COST ($/HR)	WETOX COST (M$)	CAP COST (M$)	COD REMOV (%)	THERM EFFIC (%)	NET POWER (MW)	ENERGY COST ($/GJ)
.40	50.0	5.0	232.2	263.66	.18	7.4	47.63	51.0	6.9	12.663
1.50	50.0	5.0	232.2	263.66	.18	7.4	47.63	51.0	6.9	15.017
2.60	50.0	5.0	232.2	263.66	.18	7.4	47.63	51.0	6.9	17.370
3.70	50.0	5.0	232.2	263.66	.18	7.4	47.63	51.0	6.9	19.723
4.80	50.0	5.0	232.2	263.66	.18	7.4	47.63	51.0	6.9	22.076
.40	50.0	12.5	232.2	258.88	.32	7.2	51.41	51.0	7.0	12.214
1.50	50.0	12.5	232.2	258.88	.32	7.2	51.41	51.0	7.0	14.524
2.60	50.0	12.5	232.2	258.88	.32	7.2	51.41	51.0	7.0	16.835
3.70	50.0	12.5	232.2	258.88	.32	7.2	51.41	51.0	7.0	19.144
4.80	50.0	12.5	232.2	258.88	.32	7.2	51.41	51.0	7.0	21.453
.40	50.0	20.0	232.2	254.41	.55	7.6	54.93	51.1	7.2	11.815
1.50	50.0	20.0	232.2	254.41	.55	7.6	54.93	51.1	7.2	14.084
2.60	50.0	20.0	232.2	254.41	.55	7.6	54.93	51.1	7.2	16.354
3.70	50.0	20.0	232.2	254.41	.55	7.6	54.93	51.1	7.2	18.624
4.80	50.0	20.0	232.2	254.41	.55	7.6	54.93	51.1	7.2	20.894
.40	50.0	27.5	232.2	250.25	.68	7.8	58.18	51.1	7.3	11.454
1.50	50.0	27.5	232.2	250.25	.68	7.8	58.18	51.1	7.3	13.688
2.60	50.0	27.5	232.2	250.25	.68	7.8	58.18	51.1	7.3	15.923
3.70	50.0	27.5	232.2	250.25	.68	7.8	58.18	51.1	7.3	18.157
4.80	50.0	27.5	232.2	250.25	.68	7.8	58.18	51.1	7.3	20.392
.40	50.0	35.0	232.2	246.40	.82	8.0	61.20	51.2	7.4	11.129
1.50	50.0	35.0	232.2	246.40	.82	8.0	61.20	51.2	7.4	13.332
2.60	50.0	35.0	232.2	246.40	.82	8.0	61.20	51.2	7.4	15.534
3.70	50.0	35.0	232.2	246.40	.82	8.0	61.20	51.2	7.4	17.737
4.80	50.0	35.0	232.2	246.40	.82	8.0	61.20	51.2	7.4	19.940
.40	100.0	5.0	232.2	430.88	.18	10.4	47.63	56.4	15.0	9.175
1.50	100.0	5.0	232.2	430.88	.18	10.4	47.63	56.4	15.0	10.246
2.60	100.0	5.0	232.2	430.88	.18	10.4	47.63	56.4	15.0	11.317
3.70	100.0	5.0	232.2	430.88	.18	10.4	47.63	56.4	15.0	12.389
4.80	100.0	5.0	232.2	430.88	.18	10.4	47.63	56.4	15.0	13.460
.40	100.0	12.5	232.2	421.24	.32	10.2	51.41	56.4	15.3	8.826
1.50	100.0	12.5	232.2	421.24	.32	10.2	51.41	56.4	15.3	9.879
2.60	100.0	12.5	232.2	421.24	.32	10.2	51.41	56.4	15.3	10.932
3.70	100.0	12.5	232.2	421.24	.32	10.2	51.41	56.4	15.3	11.985
4.80	100.0	12.5	232.2	421.24	.32	10.2	51.41	56.4	15.3	13.038
.40	100.0	20.0	232.2	412.32	.55	10.5	54.93	56.3	15.6	8.512
1.50	100.0	20.0	232.2	412.32	.55	10.5	54.93	56.3	15.6	9.548
2.60	100.0	20.0	232.2	412.32	.55	10.5	54.93	56.3	15.6	10.585
3.70	100.0	20.0	232.2	412.32	.55	10.5	54.93	56.3	15.6	11.622
4.80	100.0	20.0	232.2	412.32	.55	10.5	54.93	56.3	15.6	12.658
.40	100.0	27.5	232.2	404.04	.68	10.2	58.18	56.3	15.9	8.230
1.50	100.0	27.5	232.2	404.04	.68	10.2	58.18	56.3	15.9	9.252
2.60	100.0	27.5	232.2	404.04	.68	10.2	58.18	56.3	15.9	10.273
3.70	100.0	27.5	232.2	404.04	.68	10.2	58.18	56.3	15.9	11.295
4.80	100.0	27.5	232.2	404.04	.68	10.2	58.18	56.3	15.9	12.317
.40	100.0	35.0	232.2	396.36	.82	10.3	61.20	56.3	16.1	7.974
1.50	100.0	35.0	232.2	396.36	.82	10.3	61.20	56.3	16.1	8.983
2.60	100.0	35.0	232.2	396.36	.82	10.3	61.20	56.3	16.1	9.992
3.70	100.0	35.0	232.2	396.36	.82	10.3	61.20	56.3	16.1	11.000
4.80	100.0	35.0	232.2	396.36	.82	10.3	61.20	56.3	16.1	12.009
.40	150.0	5.0	232.2	598.08	.18	14.2	47.63	58.2	23.2	8.146
1.50	150.0	5.0	232.2	598.08	.18	14.2	47.63	58.2	23.2	8.840
2.60	150.0	5.0	232.2	598.08	.18	14.2	47.63	58.2	23.2	9.533
3.70	150.0	5.0	232.2	598.08	.18	14.2	47.63	58.2	23.2	10.227
4.80	150.0	5.0	232.2	598.08	.18	14.2	47.63	58.2	23.2	10.921
.40	150.0	12.5	232.2	583.65	.32	13.7	51.41	58.2	23.7	7.824

PEAT COST ($/T)	COD CONC. (G/L)	RES TIME (MIN)	REAC TEMP. (C)	OPER. COST ($/HR)	VETOX COST (M$)	CAP COST (M$)	COD REMOV. (%)	THERM EFFIC. (%)	NET POWER (MW)	ENERGY COST ($/GJ)
1.50	150.0	12.5	232.2	583.65	.32	13.7	51.41	58.2	23.7	8.506
2.60	150.0	12.5	232.2	583.65	.32	13.7	51.41	58.2	23.7	9.188
3.70	150.0	12.5	232.2	583.65	.32	13.7	51.41	58.2	23.7	9.870
4.80	150.0	12.5	232.2	583.65	.32	13.7	51.41	58.2	23.7	10.552
.40	150.0	20.0	232.2	570.24	.55	13.5	54.93	58.1	24.1	7.534
1.50	150.0	20.0	232.2	570.24	.55	13.5	54.93	58.1	24.1	8.204
2.60	150.0	20.0	232.2	570.24	.55	13.5	54.93	58.1	24.1	8.878
3.70	150.0	20.0	232.2	570.24	.55	13.5	54.93	58.1	24.1	9.550
4.80	150.0	20.0	232.2	570.24	.55	13.5	54.93	58.1	24.1	10.221
.40	150.0	27.5	232.2	557.82	.68	13.4	58.18	58.0	24.5	7.273
1.50	150.0	27.5	232.2	557.82	.68	13.4	58.18	58.0	24.5	7.936
2.60	150.0	27.5	232.2	557.82	.68	13.4	58.18	58.0	24.5	8.598
3.70	150.0	27.5	232.2	557.82	.68	13.4	58.18	58.0	24.5	9.260
4.80	150.0	27.5	232.2	557.82	.68	13.4	58.18	58.0	24.5	9.923
.40	150.0	35.0	232.2	546.30	.82	13.0	61.20	58.0	24.9	7.038
1.50	150.0	35.0	232.2	546.30	.82	13.0	61.20	58.0	24.9	7.692
2.60	150.0	35.0	232.2	546.30	.82	13.0	61.20	58.0	24.9	8.346
3.70	150.0	35.0	232.2	546.30	.82	13.0	61.20	58.0	24.9	9.000
4.80	150.0	35.0	232.2	546.30	.82	13.0	61.20	58.0	24.9	9.654
.40	50.0	5.0	251.6	246.73	.22	6.4	61.29	50.8	7.6	11.204
1.50	50.0	5.0	251.6	246.73	.22	6.4	61.29	50.8	7.6	13.419
2.60	50.0	5.0	251.6	246.73	.22	6.4	61.29	50.8	7.6	15.633
3.70	50.0	5.0	251.6	246.73	.22	6.4	61.29	50.8	7.6	17.848
4.80	50.0	5.0	251.6	246.73	.22	6.4	61.29	50.8	7.6	20.063
.40	50.0	12.5	251.6	243.13	.41	6.8	64.09	50.8	7.7	10.911
1.50	50.0	12.5	251.6	243.13	.41	6.8	64.09	50.8	7.7	13.097
2.60	50.0	12.5	251.6	243.13	.41	6.8	64.09	50.8	7.7	15.283
3.70	50.0	12.5	251.6	243.13	.41	6.8	64.09	50.8	7.7	17.469
4.80	50.0	12.5	251.6	243.13	.41	6.8	64.09	50.8	7.7	19.655
.40	50.0	20.0	251.6	239.85	.69	7.1	66.68	50.8	7.8	10.647
1.50	50.0	20.0	251.6	239.85	.69	7.1	66.68	50.8	7.8	12.808
2.60	50.0	20.0	251.6	239.85	.69	7.1	66.68	50.8	7.8	14.968
3.70	50.0	20.0	251.6	239.85	.69	7.1	66.68	50.8	7.8	17.129
4.80	50.0	20.0	251.6	239.85	.69	7.1	66.68	50.8	7.8	19.289
.40	50.0	27.5	251.6	236.74	.89	7.6	69.09	50.9	7.9	10.406
1.50	50.0	27.5	251.6	236.74	.89	7.6	69.09	50.9	7.9	12.543
2.60	50.0	27.5	251.6	236.74	.89	7.6	69.09	50.9	7.9	14.681
3.70	50.0	27.5	251.6	236.74	.89	7.6	69.09	50.9	7.9	16.818
4.80	50.0	27.5	251.6	236.74	.89	7.6	69.09	50.9	7.9	18.955
.40	50.0	35.0	251.6	233.86	1.08	8.0	71.32	50.9	8.0	10.187
1.50	50.0	35.0	251.6	233.86	1.08	8.0	71.32	50.9	8.0	12.303
2.60	50.0	35.0	251.6	233.86	1.08	8.0	71.32	50.9	8.0	14.419
3.70	50.0	35.0	251.6	233.86	1.08	8.0	71.32	50.9	8.0	16.535
4.80	50.0	35.0	251.6	233.86	1.08	8.0	71.32	50.9	8.0	18.651
.40	100.0	5.0	251.6	395.81	.22	8.7	61.29	54.0	14.5	8.004
1.50	100.0	5.0	251.6	395.81	.22	8.7	61.29	54.0	14.5	9.017
2.60	100.0	5.0	251.6	395.81	.22	8.7	61.29	54.0	14.5	10.031
3.70	100.0	5.0	251.6	395.81	.22	8.7	61.29	54.0	14.5	11.045
4.80	100.0	5.0	251.6	395.81	.22	8.7	61.29	54.0	14.5	12.058
.40	100.0	12.5	251.6	388.62	.41	8.9	64.09	54.0	14.7	7.773
1.50	100.0	12.5	251.6	388.62	.41	8.9	64.09	54.0	14.7	8.774
2.60	100.0	12.5	251.6	388.62	.41	8.9	64.09	54.0	14.7	9.774
3.70	100.0	12.5	251.6	388.62	.41	8.9	64.09	54.0	14.7	10.778
4.80	100.0	12.5	251.6	388.62	.41	8.9	64.09	54.0	14.7	11.779
.40	100.0	20.0	251.6	381.97	.69	9.1	66.68	54.0	14.9	7.564
1.50	100.0	20.0	251.6	381.97	.69	9.1	66.68	54.0	14.9	8.554

ORI

I	PEAT COST ($/T)	COD CONC. (G/L)	RES. TIME (MIN)	REAC. TEMP (C)	OPER. COST ($/HR)	WETOX COST (M$)	CAP COST (M$)	COD REMOV. (%)	THERM. EFFIC. (%)	NET POWER (MW)	ENERGY COST ($/GJ)
	2.40	100.0	20.0	251.6	381.97	.69	9.1	64.68	56.0	16.9	9.545
	3.70	100.0	20.0	251.6	381.97	.69	9.1	64.68	56.0	16.9	10.536
	4.80	100.0	20.0	251.6	381.97	.69	9.1	64.68	56.0	16.9	11.527
	.40	100.0	27.5	251.6	375.78	.89	9.5	69.09	55.9	17.1	7.373
	1.50	100.0	27.5	251.6	375.78	.89	9.5	69.09	55.9	17.1	8.354
	2.60	100.0	27.5	251.6	375.78	.89	9.5	69.09	55.9	17.1	9.335
	3.70	100.0	27.5	251.6	375.78	.89	9.5	69.09	55.9	17.1	10.316
	4.80	100.0	27.5	251.6	375.78	.89	9.5	69.09	55.9	17.1	11.297
	.40	100.0	35.0	251.6	370.03	1.08	9.8	71.32	55.9	17.3	7.199
	1.50	100.0	35.0	251.6	370.03	1.08	9.8	71.32	55.9	17.3	8.172
	2.60	100.0	35.0	251.6	370.03	1.08	9.8	71.32	55.9	17.3	9.144
	3.70	100.0	35.0	251.6	370.03	1.08	9.8	71.32	55.9	17.3	10.116
	4.80	100.0	35.0	251.6	370.03	1.08	9.8	71.32	55.9	17.3	11.088
	.40	150.0	5.0	251.6	544.87	.22	11.4	61.29	57.8	25.3	7.054
	1.50	150.0	5.0	251.6	544.87	.22	11.4	61.29	57.8	25.3	7.711
	2.60	150.0	5.0	251.6	544.87	.22	11.4	61.29	57.8	25.3	8.368
	3.70	150.0	5.0	251.6	544.87	.22	11.4	61.29	57.8	25.3	9.026
	4.80	150.0	5.0	251.6	544.87	.22	11.4	61.29	57.8	25.3	9.683
	.40	150.0	12.5	251.6	534.09	.41	11.5	64.09	57.7	25.7	6.840
	1.50	150.0	12.5	251.6	534.09	.41	11.5	64.09	57.7	25.7	7.498
	2.60	150.0	12.5	251.6	534.09	.41	11.5	64.09	57.7	25.7	8.139
	3.70	150.0	12.5	251.6	534.09	.41	11.5	64.09	57.7	25.7	8.789
	4.80	150.0	12.5	251.6	534.09	.41	11.5	64.09	57.7	25.7	9.439
	.40	150.0	20.0	251.6	524.10	.69	11.6	66.68	57.7	26.0	6.644
	1.50	150.0	20.0	251.6	524.10	.69	11.6	66.68	57.7	26.0	7.289
	2.60	150.0	20.0	251.6	524.10	.69	11.6	66.68	57.7	26.0	7.932
	3.70	150.0	20.0	251.6	524.10	.69	11.6	66.68	57.7	26.0	8.575
	4.80	150.0	20.0	251.6	524.10	.69	11.6	66.68	57.7	26.0	9.217
	.40	150.0	27.5	251.6	514.81	.89	11.8	69.09	57.6	26.3	6.469
	1.50	150.0	27.5	251.6	514.81	.89	11.8	69.09	57.6	26.3	7.104
	2.60	150.0	27.5	251.6	514.81	.89	11.8	69.09	57.6	26.3	7.743
	3.70	150.0	27.5	251.6	514.81	.89	11.8	69.09	57.6	26.3	8.379
	4.80	150.0	27.5	251.6	514.81	.89	11.8	69.09	57.6	26.3	9.016
	.40	150.0	35.0	251.6	504.22	1.08	11.7	71.32	57.6	26.4	6.309
	1.50	150.0	35.0	251.6	504.22	1.08	11.7	71.32	57.6	26.4	6.940
	2.60	150.0	35.0	251.6	504.22	1.08	11.7	71.32	57.6	26.4	7.571
	3.70	150.0	35.0	251.6	504.22	1.08	11.7	71.32	57.6	26.4	8.202
	4.80	150.0	35.0	251.6	504.22	1.08	11.7	71.32	57.6	26.4	8.833
	.40	50.0	5.0	271.0	240.48	.27	5.7	72.30	48.9	8.1	10.478
	1.50	50.0	5.0	271.0	240.48	.27	5.7	72.30	48.9	8.1	12.598
	2.60	50.0	5.0	271.0	240.48	.27	5.7	72.30	48.9	8.1	14.719
	3.70	50.0	5.0	271.0	240.48	.27	5.7	72.30	48.9	8.1	16.840
	4.80	50.0	5.0	271.0	240.48	.27	5.7	72.30	48.9	8.1	18.961
	.40	50.0	12.5	271.0	220.07	.53	6.3	74.30	48.9	8.2	9.570
	1.50	50.0	12.5	271.0	220.07	.53	6.3	74.30	48.9	8.2	11.673
	2.60	50.0	12.5	271.0	220.07	.53	6.3	74.30	48.9	8.2	13.774
	3.70	50.0	12.5	271.0	220.07	.53	6.3	74.30	48.9	8.2	15.878
	4.80	50.0	12.5	271.0	220.07	.53	6.3	74.30	48.9	8.2	17.981
	.40	50.0	20.0	271.0	217.84	.88	7.3	74.16	48.9	8.2	9.406
	1.50	50.0	20.0	271.0	217.84	.88	7.3	74.16	48.9	8.2	11.491
	2.60	50.0	20.0	271.0	217.84	.88	7.3	74.16	48.9	8.2	13.577
	3.70	50.0	20.0	271.0	217.84	.88	7.3	74.16	48.9	8.2	15.663
	4.80	50.0	20.0	271.0	217.84	.88	7.3	74.16	48.9	8.2	17.749
	.40	50.0	27.5	271.0	215.74	1.15	7.9	77.88	48.9	8.3	9.255
	1.50	50.0	27.5	271.0	215.74	1.15	7.9	77.88	48.9	8.3	11.324
	2.60	50.0	27.5	271.0	215.74	1.15	7.9	77.88	48.9	8.3	13.396

ORI

PEAT COST ($/T)	COD CONC. (G/L)	RES. TIME (MIN)	REAC TEMP. (C)	OPER. COST ($/HR)	VETOX COST (M$)	CAP COST (M$)	COD REMOV. (%)	THERM. EFFIC. (%)	NET POWER (MW)	ENERGY COST ($/GJ)
3.70	50.0	27.5	271.0	215.76	1.15	7.9	77.88	48.9	8.3	15.467
4.80	50.0	27.5	271.0	215.76	1.15	7.9	77.88	48.9	8.3	17.537
.40	50.0	35.0	271.0	213.84	1.41	8.6	79.48	48.9	8.4	9.117
1.50	50.0	35.0	271.0	213.84	1.41	8.6	79.48	48.9	8.4	11.174
2.40	50.0	35.0	271.0	213.84	1.41	8.6	79.48	48.9	8.4	13.230
3.70	50.0	35.0	271.0	213.84	1.41	8.6	79.48	48.9	8.4	15.287
4.80	50.0	35.0	271.0	213.84	1.41	8.6	79.48	48.9	8.4	17.344
.40	100.0	5.0	271.0	381.71	.27	7.4	72.30	53.9	17.4	7.431
1.50	100.0	5.0	271.0	381.71	.27	7.4	72.30	53.9	17.4	8.405
2.40	100.0	5.0	271.0	381.71	.27	7.4	72.30	53.9	17.4	9.380
3.70	100.0	5.0	271.0	381.71	.27	7.4	72.30	53.9	17.4	10.354
4.80	100.0	5.0	271.0	381.71	.27	7.4	72.30	53.9	17.4	11.328
.40	100.0	12.5	271.0	374.95	.53	7.6	74.30	53.9	17.6	7.285
1.50	100.0	12.5	271.0	374.95	.53	7.6	74.30	53.9	17.6	8.251
2.40	100.0	12.5	271.0	374.95	.53	7.6	74.30	53.9	17.6	9.218
3.70	100.0	12.5	271.0	374.95	.53	7.6	74.30	53.9	17.6	10.184
4.80	100.0	12.5	271.0	374.95	.53	7.6	74.30	53.9	17.6	11.150
.40	100.0	20.0	271.0	372.49	.88	8.5	74.14	53.8	17.8	7.150
1.50	100.0	20.0	271.0	372.49	.88	8.5	74.14	53.8	17.8	8.109
2.40	100.0	20.0	271.0	372.49	.88	8.5	74.14	53.8	17.8	9.069
3.70	100.0	20.0	271.0	372.49	.88	8.5	74.14	53.8	17.8	10.028
4.80	100.0	20.0	271.0	372.49	.88	8.5	74.14	53.8	17.8	10.987
.40	100.0	27.5	271.0	368.36	1.15	9.1	77.88	53.8	17.9	7.027
1.50	100.0	27.5	271.0	368.36	1.15	9.1	77.88	53.8	17.9	7.980
2.40	100.0	27.5	271.0	368.36	1.15	9.1	77.88	53.8	17.9	8.933
3.70	100.0	27.5	271.0	368.36	1.15	9.1	77.88	53.8	17.9	9.885
4.80	100.0	27.5	271.0	368.36	1.15	9.1	77.88	53.8	17.9	10.838
.40	100.0	35.0	271.0	364.52	1.41	9.7	79.48	53.8	18.1	4.914
1.50	100.0	35.0	271.0	364.52	1.41	9.7	79.48	53.8	18.1	7.861
2.40	100.0	35.0	271.0	364.52	1.41	9.7	79.48	53.8	18.1	8.808
3.70	100.0	35.0	271.0	364.52	1.41	9.7	79.48	53.8	18.1	9.755
4.80	100.0	35.0	271.0	364.52	1.41	9.7	79.48	53.8	18.1	10.702
.40	150.0	5.0	271.0	522.97	.27	9.2	72.30	55.6	26.8	6.523
1.50	150.0	5.0	271.0	522.97	.27	9.2	72.30	55.6	26.8	7.156
2.40	150.0	5.0	271.0	522.97	.27	9.2	72.30	55.6	26.8	7.788
3.70	150.0	5.0	271.0	522.97	.27	9.2	72.30	55.6	26.8	8.420
4.80	150.0	5.0	271.0	522.97	.27	9.2	72.30	55.6	26.8	9.053
.40	150.0	12.5	271.0	515.77	.53	9.7	74.30	55.6	27.1	6.387
1.50	150.0	12.5	271.0	515.77	.53	9.7	74.30	55.6	27.1	7.014
2.40	150.0	12.5	271.0	515.77	.53	9.7	74.30	55.6	27.1	7.642
3.70	150.0	12.5	271.0	515.77	.53	9.7	74.30	55.6	27.1	8.269
4.80	150.0	12.5	271.0	515.77	.53	9.7	74.30	55.6	27.1	8.897
.40	150.0	20.0	271.0	509.09	.88	10.5	74.14	55.5	27.3	6.242
1.50	150.0	20.0	271.0	509.09	.88	10.5	74.14	55.5	27.3	6.885
2.40	150.0	20.0	271.0	509.09	.88	10.5	74.14	55.5	27.3	7.508
3.70	150.0	20.0	271.0	509.09	.88	10.5	74.14	55.5	27.3	8.131
4.80	150.0	20.0	271.0	509.09	.88	10.5	74.14	55.5	27.3	8.754
.40	150.0	27.5	271.0	502.93	1.15	10.6	77.88	55.5	27.5	6.148
1.50	150.0	27.5	271.0	502.93	1.15	10.6	77.88	55.5	27.5	6.747
2.40	150.0	27.5	271.0	502.93	1.15	10.6	77.88	55.5	27.5	7.346
3.70	150.0	27.5	271.0	502.93	1.15	10.6	77.88	55.5	27.5	8.005
4.80	150.0	27.5	271.0	502.93	1.15	10.6	77.88	55.5	27.5	8.624
.40	150.0	35.0	271.0	497.18	1.41	11.2	79.48	55.4	27.7	6.044
1.50	150.0	35.0	271.0	497.18	1.41	11.2	79.48	55.4	27.7	6.659
2.40	150.0	35.0	271.0	497.18	1.41	11.2	79.48	55.4	27.7	7.274
3.70	150.0	35.0	271.0	497.18	1.41	11.2	79.48	55.4	27.7	7.889

PEAT COST ($/T)	COD CONC. (G/L)	RES. TIME (MIN)	REAC. TEMP. (C)	OPER COST ($/HR)	WETOX COST (M$)	CAP COST (M$)	COD REMOV (%)	THERM EFFIC (%)	NET POWER (MW)	ENERGY COST ($/GJ)
4.80	150.0	35.0	271.0	497.18	1.41	11.2	79.48	55.4	27.7	8.504

APPENDIX G

Cost Study, Case 2
Electrical Energy Generation
Through Wet Oxidation and
Anaerobic Digestion

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 1$VARS
 0K101    = 0.0,
 0K102    = .1E-01,
 0KA      = .4111E+04,
 0KB      = -.10401E+05,
 0T10     = .2322E+03,
 0RT10    = .5E+01,
 0CODIN   = .5E+02,
 0PL10    = .254E+03,
 0EXSA    = .1E+00,
 0TIN1    = .1E+02,
 0OVP     = .5E+00,
 0FR10    = .5E+02,
 0MF      = .1E+01,
 0L10     = .19E+02,
 0NSTEP   = 1,
 0UHEX1   = .204E+00,
 0HR      = .1E+02,
 0ELEC    = .5E-01,
 0DRT     = .75E+01,
 0DCOD    = .5E+02,
 0DTEM    = .194E+02,
 0DRM     = .11E+01,
 0BP      = .3E+01,
 0IR      = .18E+00,
 0LIFE    = .2E+02,
 0RM      = .4E+00,
 0ITEMP   = 2,
 0ICOD    = 3,
 0IRT     = 5,
 0K1      = .274E-02,
 0K2      = .137E-03,
 0L9      = .19E+02,
 0VN9     = .22E+03,
 0B9A     = .555E-04,
 0B9B     = .1E-03,
 0B9C     = .475E-02,
 0WALL    = .5E+00,
 0ROOF    = .15E+00,
 0PL9     = .254E+03,
 0IRM     = 5,
 0T9      = .3E+02,
 0SSA     = .75E+02,
 0DEAD    = .1E+00,
 0LFAC    = .12E+02,
 0TREAT   = .8E+00,
 0RECYC   = .2E+01,
 0H2DR    = .1E+01,
 0TAMB    = .18E+02,
 0NR9     = 0,
 0$END
 1      INPUT OPTIONS
 1$OPTS
 0IFLTH   = 1,
 0IFLCD   = 1,
 0IFLRT   = 1,
 0IFLRM   = 1,
 0IFLAD   = 1,
 0IFLEG   = 1,
 0$END
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I	PEAT COST ($/T)	COD CONC. (G/L)	RES TIME (MIN)	REAC TEMP. (C)	OPER. COST ($/HR)	WL.OX COST (M$)	CAP COST (M$)	COD REMOV. (%)	THERM. EFFIC. (%)	NET POWER (MW)	ENERGY COST ($/KWH)
	.40	50.0	5.0	232.2	229.45	.18	7.3	47.63	18.6	1.9	.140
	1.50	50.0	5.0	232.2	229.45	.18	7.3	47.63	18.6	1.9	.169
	2.60	50.0	5.0	232.2	229.45	.18	7.3	47.63	18.6	1.9	.199
	3.70	50.0	5.0	232.2	229.45	.18	7.3	47.63	18.6	1.9	.228
	4.80	50.0	5.0	232.2	229.45	.18	7.3	47.63	18.6	1.9	.258
	.40	50.0	12.5	232.2	220.25	.32	7.1	51.41	15.3	1.5	.143
	1.50	50.0	12.5	232.2	220.25	.32	7.1	51.41	15.3	1.5	.198
	2.60	50.0	12.5	232.2	220.25	.32	7.1	51.41	15.3	1.5	.234
	3.70	50.0	12.5	232.2	220.25	.32	7.1	51.41	15.3	1.5	.270
	4.80	50.0	12.5	232.2	220.25	.32	7.1	51.41	15.3	1.5	.306
	.40	50.0	20.0	232.2	211.91	.55	7.5	54.93	12.3	1.2	.194
	1.50	50.0	20.0	232.2	211.91	.55	7.5	54.93	12.3	1.2	.238
	2.60	50.0	20.0	232.2	211.91	.55	7.5	54.93	12.3	1.2	.282
	3.70	50.0	20.0	232.2	211.91	.55	7.5	54.93	12.3	1.2	.326
	4.80	50.0	20.0	232.2	211.91	.55	7.5	54.93	12.3	1.2	.370
	.40	50.0	27.5	232.2	204.15	.68	7.7	58.18	9.5	1.0	.238
	1.50	50.0	27.5	232.2	204.15	.68	7.7	58.18	9.5	1.0	.294
	2.60	50.0	27.5	232.2	204.15	.68	7.7	58.18	9.5	1.0	.350
	3.70	50.0	27.5	232.2	204.15	.68	7.7	58.18	9.5	1.0	.406
	4.80	50.0	27.5	232.2	204.15	.68	7.7	58.18	9.5	1.0	.463
	.40	50.0	35.0	232.2	196.95	.82	7.9	61.20	7.1	.7	.306
	1.50	50.0	35.0	232.2	196.95	.82	7.9	61.20	7.1	.7	.381
	2.60	50.0	35.0	232.2	196.95	.82	7.9	61.20	7.1	.7	.455
	3.70	50.0	35.0	232.2	196.95	.82	7.9	61.20	7.1	.7	.530
	4.80	50.0	35.0	232.2	196.95	.82	7.9	61.20	7.1	.7	.604
	.40	100.0	5.0	232.2	350.50	.18	12.0	47.63	12.7	2.6	.149
	1.50	100.0	5.0	232.2	350.50	.18	12.0	47.63	12.7	2.6	.170
	2.60	100.0	5.0	232.2	350.50	.18	12.0	47.63	12.7	2.6	.191
	3.70	100.0	5.0	232.2	350.50	.18	12.0	47.63	12.7	2.6	.213
	4.80	100.0	5.0	232.2	350.50	.18	12.0	47.63	12.7	2.6	.234
	.40	100.0	12.5	232.2	333.29	.32	11.8	51.41	12.0	2.5	.149
	1.50	100.0	12.5	232.2	333.29	.32	11.8	51.41	12.0	2.5	.171
	2.60	100.0	12.5	232.2	333.29	.32	11.8	51.41	12.0	2.5	.193
	3.70	100.0	12.5	232.2	333.29	.32	11.8	51.41	12.0	2.5	.215
	4.80	100.0	12.5	232.2	333.29	.32	11.8	51.41	12.0	2.5	.238
	.40	100.0	20.0	232.2	317.33	.55	12.1	54.93	11.4	2.4	.149
	1.50	100.0	20.0	232.2	317.33	.55	12.1	54.93	11.4	2.4	.172
	2.60	100.0	20.0	232.2	317.33	.55	12.1	54.93	11.4	2.4	.195
	3.70	100.0	20.0	232.2	317.33	.55	12.1	54.93	11.4	2.4	.218
	4.80	100.0	20.0	232.2	317.33	.55	12.1	54.93	11.4	2.4	.242
	.40	100.0	27.5	232.2	302.53	.68	11.9	58.18	10.9	2.3	.148
	1.50	100.0	27.5	232.2	302.53	.68	11.9	58.18	10.9	2.3	.173
	2.60	100.0	27.5	232.2	302.53	.68	11.9	58.18	10.9	2.3	.197
	3.70	100.0	27.5	232.2	302.53	.68	11.9	58.18	10.9	2.3	.221
	4.80	100.0	27.5	232.2	302.53	.68	11.9	58.18	10.9	2.3	.245
	.40	100.0	35.0	232.2	288.48	.82	11.9	61.20	8.8	1.9	.173
	1.50	100.0	35.0	232.2	288.48	.82	11.9	61.20	8.8	1.9	.202
	2.60	100.0	35.0	232.2	288.48	.82	11.9	61.20	8.8	1.9	.232
	3.70	100.0	35.0	232.2	288.48	.82	11.9	61.20	8.8	1.9	.261
	4.80	100.0	35.0	232.2	288.48	.82	11.9	61.20	8.8	1.9	.291
	.40	150.0	5.0	232.2	470.94	.18	16.5	47.63	9.4	2.9	.175
	1.50	150.0	5.0	232.2	470.94	.18	16.5	47.63	9.4	2.9	.194
	2.60	150.0	5.0	232.2	470.94	.18	16.5	47.63	9.4	2.9	.213
	3.70	150.0	5.0	232.2	470.94	.18	16.5	47.63	9.4	2.9	.232
	4.80	150.0	5.0	232.2	470.94	.18	16.5	47.63	9.4	2.9	.251
	.40	150.0	12.5	232.2	445.12	.32	16.0	51.41	8.7	2.7	.177

ERCO

PEAT COST ($/T)	COD CONC. (G/L)	RES TIME (MIN)	REAC TEMP (C)	OPER COST ($/HR)	WETOX COST (M$)	CAP COST (M$)	COD REMOV. (%)	THERM. EFFIC (%)	NET POWER (MW)	ENERGY COST ($/KWH)
1.50	150.0	12.5	232.2	445.12	.32	16.0	51.41	8.7	2.7	.197
2.40	150.0	12.5	232.2	445.12	.32	16.0	51.41	8.7	2.7	.217
3.70	150.0	12.5	232.2	445.12	.32	16.0	51.41	8.7	2.7	.237
4.80	150.0	12.5	232.2	445.12	.32	16.0	51.41	8.7	2.7	.257
.40	150.0	20.0	232.2	421.18	.55	15.8	54.93	8.1	2.6	.178
1.50	150.0	20.0	232.2	421.18	.55	15.8	54.93	8.1	2.6	.200
2.40	150.0	20.0	232.2	421.18	.55	15.8	54.93	8.1	2.6	.221
3.70	150.0	20.0	232.2	421.18	.55	15.8	54.93	8.1	2.6	.242
4.80	150.0	20.0	232.2	421.18	.55	15.8	54.93	8.1	2.6	.263
.40	150.0	27.5	232.2	398.96	.68	15.8	58.18	7.5	2.4	.180
1.50	150.0	27.5	232.2	398.96	.68	15.8	58.18	7.5	2.4	.202
2.40	150.0	27.5	232.2	398.96	.68	15.8	58.18	7.5	2.4	.225
3.70	150.0	27.5	232.2	398.96	.68	15.8	58.18	7.5	2.4	.248
4.80	150.0	27.5	232.2	398.96	.68	15.8	58.18	7.5	2.4	.270
.40	150.0	35.0	232.2	378.35	.82	15.4	61.20	7.0	2.3	.181
1.50	150.0	35.0	232.2	378.35	.82	15.4	61.20	7.0	2.3	.205
2.40	150.0	35.0	232.2	378.35	.82	15.4	61.20	7.0	2.3	.229
3.70	150.0	35.0	232.2	378.35	.82	15.4	61.20	7.0	2.3	.253
4.80	150.0	35.0	232.2	378.35	.82	15.4	61.20	7.0	2.3	.277
.40	50.0	5.0	251.6	196.74	.22	6.1	61.29	6.7	.7	.313
1.50	50.0	5.0	251.6	196.74	.22	6.1	61.29	6.7	.7	.390
2.40	50.0	5.0	251.6	196.74	.22	6.1	61.29	6.7	.7	.466
3.70	50.0	5.0	251.6	196.74	.22	6.1	61.29	6.7	.7	.542
4.80	50.0	5.0	251.6	196.74	.22	6.1	61.29	6.7	.7	.619
.40	50.0	12.5	251.6	190.06	.41	6.5	64.09	4.5	.5	.435
1.50	50.0	12.5	251.6	190.06	.41	6.5	64.09	4.5	.5	.545
2.40	50.0	12.5	251.6	190.06	.41	6.5	64.09	4.5	.5	.654
3.70	50.0	12.5	251.6	190.06	.41	6.5	64.09	4.5	.5	.764
4.80	50.0	12.5	251.6	190.06	.41	6.5	64.09	4.5	.5	.873
.40	50.0	20.0	251.6	183.85	.69	6.8	66.68	2.5	.3	.701
1.50	50.0	20.0	251.6	183.85	.69	6.8	66.68	2.5	.3	.882
2.40	50.0	20.0	251.6	183.85	.69	6.8	66.68	2.5	.3	1.064
3.70	50.0	20.0	251.6	183.85	.69	6.8	66.68	2.5	.3	1.245
4.80	50.0	20.0	251.6	183.85	.69	6.8	66.68	2.5	.3	1.426
.40	50.0	27.5	251.6	178.07	.89	7.2	69.09	.6	.1	1.718
1.50	50.0	27.5	251.6	178.07	.89	7.2	69.09	.6	.1	2.176
2.40	50.0	27.5	251.6	178.07	.89	7.2	69.09	.6	.1	2.633
3.70	50.0	27.5	251.6	178.07	.89	7.2	69.09	.6	.1	3.091
4.80	50.0	27.5	251.6	178.07	.89	7.2	69.09	.6	.1	3.549
.40	50.0	35.0	232.2	NO NET POWER AVAILABLE						
1.50	50.0	35.0	232.2	NO NET POWER AVAILABLE						
2.40	50.0	35.0	232.2	NO NET POWER AVAILABLE						
3.70	50.0	35.0	232.2	NO NET POWER AVAILABLE						
4.80	50.0	35.0	232.2	NO NET POWER AVAILABLE						
.40	100.0	5.0	251.6	288.08	.22	10.1	61.29	8.5	1.9	.173
1.50	100.0	5.0	251.6	288.08	.22	10.1	61.29	8.5	1.9	.202
2.40	100.0	5.0	251.6	288.08	.22	10.1	61.29	8.5	1.9	.232
3.70	100.0	5.0	251.6	288.08	.22	10.1	61.29	8.5	1.9	.261
4.80	100.0	5.0	251.6	288.08	.22	10.1	61.29	8.5	1.9	.291
.40	100.0	12.5	251.6	274.95	.41	10.3	64.09	6.1	1.4	.223
1.50	100.0	12.5	251.6	274.95	.41	10.3	64.09	6.1	1.4	.263
2.40	100.0	12.5	251.6	274.95	.41	10.3	64.09	6.1	1.4	.303
3.70	100.0	12.5	251.6	274.95	.41	10.3	64.09	6.1	1.4	.343
4.80	100.0	12.5	251.6	274.95	.41	10.3	64.09	6.1	1.4	.383
.40	100.0	20.0	251.6	262.74	.69	10.4	66.68	3.9	.9	.314
1.50	100.0	20.0	251.6	262.74	.69	10.4	66.68	3.9	.9	.373

PEAT COST ($/T)	COD CONC (G/L)	RES TIME (MIN)	REAC TEMP (C)	OPER COST ($/HR)	WETOX COST (M$)	CAP COST (M$)	COD REMOV (%)	THERM EFFIC (%)	NET POWER (MW)	ENERGY COST ($/KWH)
2.40	100.0	20.0	251.6	262.74	.69	10.4	66.68	3.9	.9	.432
3.70	100.0	20.0	251.6	262.74	.69	10.4	66.68	3.9	.9	.490
4.80	100.0	20.0	251.6	262.74	.69	10.4	66.68	3.9	.9	.549
.40	100.0	27.5	251.6	251.41	.89	10.6	69.09	1.8	.5	.526
1.50	100.0	27.5	251.6	251.41	.89	10.6	69.09	1.8	.5	.628
2.40	100.0	27.5	251.6	251.41	.89	10.6	69.09	1.8	.5	.730
3.70	100.0	27.5	251.6	251.41	.89	10.6	69.09	1.8	.5	.832
4.80	100.0	27.5	251.6	251.41	.89	10.6	69.09	1.8	.5	.934
.40	100.0	35.0	251.6	240.88	1.08	10.9	71.32	0	.2	1.563
1.50	100.0	35.0	251.6	240.88	1.08	10.9	71.32	0	.2	1.879
2.40	100.0	35.0	251.6	240.88	1.08	10.9	71.32	0	.2	2.194
3.70	100.0	35.0	251.6	240.88	1.08	10.9	71.32	0	.2	2.510
4.80	100.0	35.0	251.6	240.88	1.08	10.9	71.32	0	.2	2.826
.40	150.0	5.0	251.6	378.02	.22	13.7	61.29	7.9	2.4	.158
1.50	150.0	5.0	251.6	378.02	.22	13.7	61.29	7.9	2.4	.178
2.40	150.0	5.0	251.6	378.02	.22	13.7	61.29	7.9	2.4	.199
3.70	150.0	5.0	251.6	378.02	.22	13.7	61.29	7.9	2.4	.220
4.80	150.0	5.0	251.6	378.02	.22	13.7	61.29	7.9	2.4	.241
.40	150.0	12.5	251.6	358.84	.41	13.9	64.09	6.9	2.4	.166
1.50	150.0	12.5	251.6	358.84	.41	13.9	64.09	6.9	2.4	.189
2.40	150.0	12.5	251.6	358.84	.41	13.9	64.09	6.9	2.4	.212
3.70	150.0	12.5	251.6	358.84	.41	13.9	64.09	6.9	2.4	.235
4.80	150.0	12.5	251.6	358.84	.41	13.9	64.09	6.9	2.4	.258
.40	150.0	20.0	251.6	340.66	.69	13.8	66.68	4.6	1.7	.224
1.50	150.0	20.0	251.6	340.66	.69	13.8	66.68	4.6	1.7	.257
2.40	150.0	20.0	251.6	340.66	.69	13.8	66.68	4.6	1.7	.289
3.70	150.0	20.0	251.6	340.66	.69	13.8	66.68	4.6	1.7	.322
4.80	150.0	20.0	251.6	340.66	.69	13.8	66.68	4.6	1.7	.355
.40	150.0	27.5	251.6	323.79	.89	13.9	69.09	2.5	1.0	.342
1.50	150.0	27.5	251.6	323.79	.89	13.9	69.09	2.5	1.0	.395
2.40	150.0	27.5	251.6	323.79	.89	13.9	69.09	2.5	1.0	.447
3.70	150.0	27.5	251.6	323.79	.89	13.9	69.09	2.5	1.0	.500
4.80	150.0	27.5	251.6	323.79	.89	13.9	69.09	2.5	1.0	.552
.40	150.0	35.0	251.6	308.12	1.08	13.6	71.32	.6	.5	.723
1.50	150.0	35.0	251.6	308.12	1.08	13.6	71.32	.6	.5	.839
2.40	150.0	35.0	251.6	308.12	1.08	13.6	71.32	.6	.5	.955
3.70	150.0	35.0	251.6	308.12	1.08	13.6	71.32	.6	.5	1.071
4.80	150.0	35.0	251.6	308.12	1.08	13.6	71.32	.6	.5	1.187

No net power available @ 271°C reactor temperature

APPENDIX H

Cost Study, Case 3
Solid Fuel Production Through
Partial Oxidation, Dewatering,
Anaerobic Digestion and Thermal Drying

```
&VARS
 GK102    =  .1E-01,
 GKA      =  .4111E+04,
 GKB      =  -.10401E+05,
 GTI0     =  .204E+03,
 GRTI0    =  .1E+03,
 GCODIN   =  .5E+02,
 GPLI0    =  .154E+03,
 GEXSA    =  .1E+00,
 GTINI    =  .1E+01,
 GOVP     =  .5E+00,
 GFRI0    =  .5E+02,
 GMF      =  .1E+01,
 GLI0     =  .19E+02,
 GNSTEP   =  1.
 GUHEXI   =  .204E+00,
 GHR      =  .1E+02,
 GELEC    =  .5E-01,
 GDRT     =  .5E+01,
 GDCOD    =  .25E+01,
 GDTEM    =  .15E+02,
 GDRH     =  .8E+00,
 GBP      =  .3E+01,
 GIR      =  .10E+00,
 GLIFE    =  .2E+02,
 GRM      =  .4E+00,
 GITEMP   =  1.
 GICOD    =  5.
 GIRT     =  1.
 GK1      =  .274E-02,
 GK2      =  .137E-03,
 GL9      =  .19E+02,
 GVN9     =  .22E+03,
 GB9A     =  .555E-04,
 GB9B     =  .1E-03,
 GB9C     =  .475E-02,
 GWALL    =  .5E+00,
 GROOF    =  .15E+00,
 GPL9     =  .254E+03,
 GIRH     =  4.
 GT9      =  .3E+02,
 GSSA     =  .75E+02,
 GDEAD    =  .1E+00,
 GLFAC    =  .12E+02,
 GTREAT   =  .8E+00,
 GRECYC   =  .2E+01,
 GH2DR    =  .1E+01,
 GTAMB    =  .10E+02,
 GNR9     =  0.
 GSOLU    =  .135E+00,
 GSREC    =  .416E+00,
 &END
&OPTS
 GIFLTH   =  0.
 GIFLCD   =  1.
 GIFLRT   =  0.
 GIFLRH   =  1.
 GIFLAD   =  1.
 GIFLEG   =  0.
 &END
```

PEAT COST ($/T)	COD CONC (G/L)	RES. TIME (MIN)	REAC TEMP (C)	STEAM REQU (T/HR)	HEAT OUT (GJ/HR)	GAS PROD (GJ/HR)	PEAT PROD (T/HR)	MOIST CONT (%)	CAPITAL COST ($M)	PEAT COST ($/T)	ENERGY COST ($/GJ)
.40	50.0	10.0	204.0	16.42	8.8	2.2	1.1	32.2	8.29	158.55	7.27
1.20	50.0	10.0	204.0	16.42	8.8	2.2	1.1	32.2	8.29	194.91	8.94
2.00	50.0	10.0	204.0	16.42	8.8	2.2	1.1	32.2	8.29	231.27	10.61
2.80	50.0	10.0	204.0	16.42	8.8	2.2	1.1	32.2	8.29	267.64	12.28
3.60	50.0	10.0	204.0	16.42	8.8	2.2	1.1	32.2	8.29	304.00	13.95
4.40	50.0	10.0	204.0	16.42	8.8	2.2	1.1	32.2	8.29	340.37	15.61
.40	75.0	10.0	204.0	16.37	12.9	3.3	1.7	32.5	8.15	119.40	5.48
1.20	75.0	10.0	204.0	16.37	12.9	3.3	1.7	32.5	8.15	143.44	6.59
2.00	75.0	10.0	204.0	16.37	12.9	3.3	1.7	32.5	8.15	167.89	7.70
2.80	75.0	10.0	204.0	16.37	12.9	3.3	1.7	32.5	8.15	192.13	8.81
3.60	75.0	10.0	204.0	16.37	12.9	3.3	1.7	32.5	8.15	216.37	9.93
4.40	75.0	10.0	204.0	16.37	12.9	3.3	1.7	32.5	8.15	240.61	11.04
.40	100.0	10.0	204.0	16.12	17.0	4.3	2.2	32.7	8.46	99.42	4.57
1.20	100.0	10.0	204.0	16.12	17.0	4.3	2.2	32.7	8.46	117.80	5.40
2.00	100.0	10.0	204.0	16.12	17.0	4.3	2.2	32.7	8.46	135.98	6.24
2.80	100.0	10.0	204.0	16.12	17.0	4.3	2.2	32.7	8.46	154.14	7.07
3.60	100.0	10.0	204.0	16.12	17.0	4.3	2.2	32.7	8.46	172.35	7.91
4.40	100.0	10.0	204.0	16.12	17.0	4.3	2.2	32.7	8.46	190.53	8.74
.40	125.0	10.0	204.0	15.87	21.1	5.3	2.8	33.0	8.52	87.70	4.02
1.20	125.0	10.0	204.0	15.87	21.1	5.3	2.8	33.0	8.52	102.24	4.69
2.00	125.0	10.0	204.0	15.87	21.1	5.3	2.8	33.0	8.52	116.79	5.36
2.80	125.0	10.0	204.0	15.87	21.1	5.3	2.8	33.0	8.52	131.34	6.03
3.60	125.0	10.0	204.0	15.87	21.1	5.3	2.8	33.0	8.52	145.88	6.69
4.40	125.0	10.0	204.0	15.87	21.1	5.3	2.8	33.0	8.52	160.43	7.36
.40	150.0	10.0	204.0	15.62	25.2	6.3	3.3	33.3	8.65	85.41	3.92
1.20	150.0	10.0	204.0	15.62	25.2	6.3	3.3	33.3	8.65	97.53	4.47
2.00	150.0	10.0	204.0	15.62	25.2	6.3	3.3	33.3	8.65	109.66	5.03
2.80	150.0	10.0	204.0	15.62	25.2	6.3	3.3	33.3	8.65	121.78	5.59
3.60	150.0	10.0	204.0	15.62	25.2	6.3	3.3	33.3	8.65	133.90	6.14
4.40	150.0	10.0	204.0	15.62	25.2	6.3	3.3	33.3	8.65	146.02	6.70

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